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The Use of Microtube Technology in Smart Devices

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OUTLINE:

INTRODUCTION

Background

Microtubes are very small diameter tubes (in the nanometer and micron range) with very high aspect ratios that can be made from practically any material with any combination of cross-sectional and axial shapes desired. In smart structures, these microscopic tubes can function as sensors and actuators, as well as components of fluidic logic systems. In many technological fields including smart structures, Microtube

Technology enables the fabrication of components and devices that have to date been impossible to produce, offers a lower cost route for the fabrication of some current products, and provides the opportunity to miniaturize numerous components and devices that are currently in existence.

In recent years there has been tremendous interest in miniaturization due to the high payoff involved. The most graphic example that can be cited has occurred in the electronics industry which only 50 years ago relied exclusively on the vacuum tube for numerous functions. The advent of the transistor in 1947 and its gradual replacement of the vacuum tube started a revolution in miniaturization that was inconceivable at the time of its invention and not fully recognized even many years later.

Miniaturization, resulting in the possibility for billions of transistors to occupy the volume of a vacuum tube or the first transistor, was not the only result. The subsequent spin-off developments in allied areas, such as integrated circuits and the microprocessor, have spawned entirely new fields of technology. It is quite likely that other areas are now poised for revolutionary developments that parallel those that have occurred in the electronics industry since the advent of the first transistor.

These areas would include microelectromechanical systems (MEMS) and closely related fields, such as micro-fluidics and micro-optical systems. Currently, these technologies involve micro-machining on a silicon chip to produce numerous types of devices, such as, sensors, detectors, gears, engines, actuators, valves, pumps, motors, and mirrors on the micron scale. The first commercial product to arise from MEMS was the accelerometer manufactured as a sensor for air-bag actuation. On the market today, there are also micro-fluidic devices, mechanical resonators, biosensors for glucose, and disposable blood pressure sensors that are inserted into the body.

The vast majority of microsystems are made almost exclusively on planar surfaces using technology developed to fabricate electronic integrated circuits. That is, the fabrication of these devices takes place on a silicon wafer and the device is formed layer-by-layer with standard clean-room techniques that include the use of electron beams or photolithography, thin-film deposition, and wet or dry etching (both isotropic and anisotropic). There are three variations of this conventional electronic chip technology that can be used, for example, to make three-dimensional structures with high aspect ratios and suspended beams. These include the LIGA (Lithographie, Galvanoformung, Abformung) Process (1-2), the Hexsil Process (3) and SCREAM (Single Crystal Reactive Etching And Metallization) Process (4). The technique most employed is the LIGA process, which was developed specifically for MEMS-type applications and is able to construct and metallize high-aspect-ratio micro-features. This is done by applying and exposing to synchrotron radiation a very thick X-ray sensitive photo-resist layer. Features of up to 600 microns in height and with aspect ratios of 300 to 1 can be fabricated by this technique making truly ~~3~~ three-dimensional objects. The Hexsil process uses a mold with a silicon dioxide sacrificial layer to form polysilicon structures that are released by removing the silicon dioxide film. A third approach is the SCREAM bulk micromachining process, which is able to fabricate high-aspect-ratio single crystal silicon suspended microstructures from a silicon wafer using anisotropic reactive ion etching. It should be noted however that like the conventional technique used to make electronic circuits, all these variations use a layered approach starting on a flat surface.

In addition, it needs to be stated that there are some disadvantages to the conventional electronic chip fabrication technique and its modifications even though there have been numerous and very innovative successes using these silicon wafer-based technologies. This is due to the fact that these technologies require the building-up of many layers of different materials as well as surface and bulk micro-machining which leads to some very difficult material science problems that have to be solved. These include differential etching and laying down one material without damaging a previous layer. In addition, there are the problems associated with interconnecting layers in a chip with different function. An example of this would be a micro-fluidic device in which there are both fluidic and electronic functions. Clearly, there are numerous materials issues central to this technology.

There are other technologies available that, like conventional lithography, are able to construct or replicate microscopic features on a flat surface. These approaches include imprint lithography involving compression molding (5), laser (6-8), ion beam (9), and electron beam (10) micro-machining, soft lithography (11), writing features into the surface using an atomic force microscope (12-13), and very limited application of deposition using a scanning tunneling microscope (14-15). The majority of these technologies will not be discussed in detail because there is not a close link with Microtube Technology.

In addition to the processing problems mentioned above, there are other limitations inherently associated with conventional lithographic techniques that are based on planar silicon. For example, in some applications such as those that involve surface tension in fluidics, it is important to have a circular cross-section. However, it is impossible to make a perfectly round tube or channel on a chip with conventional technology. Instead channels on the wafer surface are made by etching a trench and then covering the trench with a plate (16-17). This process can only produce angled channels such as those with a square, rectangular, or triangular cross-section. Because of the limitations already mentioned, we would heartily agree with Wise and Najafi in their review of micro-fabrication technology (18) when they stated "The planar nature of silicon technology is a major limitation for many future systems, including micro-valves and pumps."

In the literature, there are at least two technologies in addition to microtubes that remove micro-fabrication from the flatland of the wafer. One makes use of "soft lithography" while the other utilizes laser-assisted chemical vapor deposition (LCVD). "Soft lithography" was conceived and developed by Whitesides' outstanding group at Harvard and encompasses a series of related very novel technologies which include micro-contact printing, micro-molding, and micro-molding in capillaries (11). These technologies are able fabricate structures from several different materials on flat as well as curved surfaces. By example, structures can be fabricated using micro-contact printing by first making a stamp with the desired features. This stamp, which is usually made from poly(dimethylsiloxane) (PDMS) has raised features placed on the surface by

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photolithographic techniques. The raised features are then "inked" with an alkanethiol and then brought into contact with a gold-coated surface, for example, by rolling the curved surface over the stamp. The gold is then etched where there is no self-assembled monolayer of alkanethiolate. Features as small as 200 nm can be formed with this technique. However, it should be mentioned that the microstructures produced by this technique are the same as those produced by standard techniques with the exception that the starting surface need not be flat. With these techniques sub-micron features can be fabricated on flat or curved substrates using materials, such as, metals (19), polymers (20), and carbon (21). In addition, these technologies can be used to make truly three-dimensional free-standing objects (22-23).

Another step away from the standard planar silicon technology is the LCVD process (24-25) which is able to "write in space" producing three-dimensional micro-systems. With this process two intersecting laser beams are brought to focus in a very small volume in a low pressure chamber. The surface of the substrate on which deposition is to occur is brought to the focal point of the lasers. The power to the lasers is adjusted so that deposition from the gas phase occurs only at the intersection of the beams. As deposition occurs on the substrate surface, it is pulled away from the focal point. Under computer control, the substrate can be manipulated so that complex free-standing three-dimensional micro-structures can be fabricated.

In addition to LCVD and soft lithography, only microtube technology offers the possibility of truly ~~3~~three-dimensional non-planar micro-systems. However, in contrast to these two technologies, microtube technology also offers the ability to make microdevices out of practically any material since the technology is not limited by electrodeposition or the availability of CVD precursor materials. In addition, in contrast to these other technologies, microtube technology not only provides the opportunity to make tubing, but also to make it in a variety of cross-sectional and axial shapes that can be used to miniaturize systems, connect components, and fabricate components or systems that are currently not possible to produce.

Microscopic and Nanoscopic Tubes and Tubules

Commercially, tubing is extruded, drawn, pultruded, or rolled and welded which limits the types of materials that can be used for ultra-small tubes as well as their ultimate internal diameters. In addition it is not currently possible to control the wall thickness, internal diameter, or the surface roughness of the inner wall of these tubes to a fraction of a micron with these techniques. Using conventional techniques, ceramic tubes are currently available only as small as 1 mm ID. Copper tubing can be obtained as small as 0.05 mm ID, polyimide tubing is fabricated as small as 50 microns ID and quartz tubing is drawn down as small as 2 microns ID. This means that quartz is the only tubing commercially available that is less than 10 microns in internal diameter. This quartz tubing is used principally for chromatographic applications.

There are, however, other sources of small tubing which are presently at various stages of research and development. For some time several groups have been using lipids as templates (26-28) in order to fabricate sub-micron diameter tubing. These tubes are made by using an electroless deposition technique to metallize a tubular lipid structure formed from a Langmuir-Blodgett film. Lipid templated tubes are very uniform in diameter, which is fixed at ~0.5 microns by the lipid structure. Lengths to 100 microns have been obtained with this technique which is extremely expensive due to the cost of the raw materials.

Other groups are making sub-micron diameter tubules using a membrane-based synthetic approach. This method involves the deposition of the desired tubule material within the cylindrical pores of a nanoporous membrane. Commercial "track-etch" polymeric membranes as well as anodic aluminum oxide films have been used as the porous substrate. The aluminum oxide, which is electrochemically etched, has been the preferred substrate because pores of uniform diameter can be made from 5-1000 nm. From the liquid phase, Martin (29-31) polymerized electrically conductive polymers and electro-chemically deposited metal in the pore structure of the membrane. Kyotani et al (32-33) have deposited pyrolytic carbon inside the pores of the same type of alumina substrate. In each case, after the inside walls of the porous membrane are covered to the desired thickness, the porous membrane is dissolved leaving the tubules. A variation of this technique, used by Hoyer (34-35) to form semiconductor (CdS, TiO_2 and WO_3) nanotubes, includes an additional step. Instead of coating the pore wall directly to form the tubule, he fills the pore with a sacrificial material, solvates the membrane and then coats the sacrificial material with the material for the nanotube wall. The sacrificial material is finally removed to form the nanotube. As with the lipid process, all the tubules formed by this process in a single membrane are uniform in diameter, length and thickness. But in contrast to the lipid process the diameter of the tubules can be varied by the extent of oxidation of the aluminum substrate. Although diameters can be varied with this process, it should be clear that these tubules are limited in length to the thickness of the porous membrane. In addition, the wall thickness is also limited in that the sum of the inside tubule diameter and two times the wall thickness is equal to the starting pore diameter.

Using a sol-gel method, tubules can be made in about the same diameter range as with the membrane approach. By hydrolyzing tetraethlyorthosilicate at room temperature in a mixture of ethanol, ammonia, water and tartaric acid, Nakamura and Matsui (36) were able to make silica tubes with both square and round interiors. The tubules produced by this technique had lengths up to 300 microns while the interior diameter of the tubes ranged from 0.02 to 0.8 microns. By introducing minute bubbles into the sol, hollow TiO_2 fibers with internal diameters up to 100 microns have also been made (37) using the sol-gel approach.

On an even smaller scale, nanotubules are fabricated using a number of very different techniques. The most well known tube in this category is the carbon "buckytube" that is a cousin of the C_{60} buckyball (38-42). Since carbon nanotubes were first observed as a by-product in C_{60} production, the method of C_{60} formation using an arc-discharge plasma was modified to enhance nanotube production. The process produced tubules with the internal diameter in the range 1-30 nanometers. These tubules are also limited in length to about 20 microns. Similar nanotubes of BN (43), B_3C, and BC_2N (44) have been made by a very similar arc discharge process. In addition, nanotubes of other compositions (45-46) have been prepared using carbon nanotubes as a substrate for conversion or deposition.

An alternative technique to manufacture carbon tubes with nanometer diameters has been known to the carbon community for decades through the work of Bacon, Baker and others (47-50). The process produces a hollow catalytic carbon fiber through the pyrolysis of a hydrocarbon gas over a catalyst particle. The fibers, which vary in diameter from 1 nm to 0.1 micron have lengths up to centimeters, can either be grown hollow or with an amorphous center that can be removed by catalytic oxidation after a fiber is formed.

Other nanoscale tubules with diameters both slightly larger and smaller than buckytubes have been made from bacteria and components of cytoskeletons as well as by direct chemical syntheses. Chow and others (51) isolated and purified nanoscale protein tubules called rhapidosomes from the bacterium *Aquaspirillum itersonii*. After the rhapidosomes were metallized by electroless deposition and the bacterium were removed, metal tubules of approximately 17 nm in diameter and 400 nm in length were produced. Using a similar metallization technique, metal tubes have been fabricated (52) with inner diameters of 25 nm using biological microtubules as templates. These microtubules, which are protein filaments with outer diameters of 25 nm and lengths measured in microns, are components of the cytoskeletons of eukaryotic cells. In contrast to tubules produced from biological templates, the tubules produced by direct chemical synthesis involve using the technique of molecular self-assembly. Some of the nanotubules that fall into this category are those made from cyclic peptides (53) and cyclodextrins (54), and bolaamphiphiles (55). Cyclic peptide nanotubules have an internal diameter of 0.8 nm and can be made several microns in length. Other self-assembled nanotubules with internal diameters from 0.45 to 0.85 nm have been synthesized from cyclodextrins (54,56) in lengths in the tens of nanometers.

Although it is clear that individual nanotubules are currently useful for certain applications, such as, encapsulation, reinforcement, or as scanning probe microscope tips (57), it is not obvious how individual nanotubules can be observed and economically manipulated for use in devices other than by using a scanning probe microscope (58). Until this problem is solved, the future of individual nanotubes in devices is uncertain. However, this problem can be circumvented if the nanotubules are part of a larger body such as in an array.

If oriented groups or arrays of sub-micron to micron diameter tubes or channels perpendicular to the surface of the wafer or device are desired, there are at least four means available to make them. Using the technique described above for making anodic porous alumina, a two step replication process (59) can be used to fabricate a highly ordered honeycomb nanohole array from gold or platinum. The metal hole array is from 1-3 micron thick with holes 70 nanometers in diameter. For smaller tubes or channels, a technique (60) has recently been developed to draw down bundles of quartz tubes to form an array. This process produces a hexagonal array of glass tubes each as small as 33 nm in diameter. This translates to a density of 3×10^{10} channels per square centimeter. Even smaller regular arrays of channels can be synthesized by a liquid crystal template mechanism (61-62). In this process, aluminum silicate gels are calcined in the presence of surfactants to produce channels with diameters of 2-10 nanometers. Finally, channels of ~4 nanometers in cross-section can be produced (63) perpendicular to the surface of an amorphous silica film by forming hematite crystals in a Fe-Si-O film and then etching away the hematite crystals.

Finally, it should be mentioned that several technologies exist to make channels or layers of channels of desired orientation in solid objects. These technologies are another spin-off of the photolithography process used for integrated circuits. On a two-dimensional plane, channels that range in size from tens to hundreds of microns in width and depth have been fabricated (16-17) on the surface of silicon wafers using standard micro-photo-lithographic techniques. The forming of microscopic channels and holes in other materials has its origin in the rocket propulsion community in 1964. Work at Aerojet Inc. (64) produced metallic injectors and cooling channels in metallic parts using a process that included photo-lithographic etching of thin metallic platelets and stacking of the platelets followed by the diffusion bonding of the platelets to form a solid metallic object with micron-sized channels. The group at Aerojet has recently modified their technique for use with silicon nitride. Variations on this technique include electrochemical micro-machining and sheet architecture technology.

Electrochemical micro-machining (65-66) avoids the generation of toxic waste from acid etching by making the thin metal part covered with exposed photoresist the anode in an electrochemical cell using a non-toxic salt solution as the electrolyte. Sheet architecture technology (67) developed at Pacific Northwest National laboratory is used to fabricate numerous microscopic chemical and thermal systems, such as, reactors, heat pumps, heat exchangers and heat absorbers. These devices may consist of a single photo-lithographically etched or laser-machined laminate with a cover bonded to seal the channels as described above or may consist of multiple layers of plastic or metal laminates bonded together.

It is quite apparent from this brief and incomplete review, that a number of very novel and innovative approaches have been used to make microsystems as well as tubes and channels with diameters in the range of nanometers to microns. In the next section, the basics of microtube technology which complements these other technologies will be discussed.

AFRL MICROTUBE TECHNOLOGY

Properties and production of microtubes

Except for self-assembled tubules, the microtube technology developed at the Propulsion Directorate of the Air Force Research Laboratory (AFRL) is able to produce tubes in the size range of all the other techniques cited. In contrast to tubing currently on the market and the sub-micron laboratory scale tubing mentioned above, microtubes can be made from practically any material (including smart materials) with precisely-controlled composition, diameter, and wall thickness in a great range of lengths. In addition, this technology is able to produce tubes with a great diversity of axial and cross-sectional geometries With most materials there is no upper diameter limit, and with practically any material, internal diameters of greater than 5 microns are possible. In addition, for materials that can survive temperatures greater than 400°C, tubes can be made as small as 5 nanometers using the same process.

To date, tubes have been made from metals (copper, nickel, aluminum, gold, platinum, silver), ceramics (silicon carbide, carbon, silicon nitride, sapphire), glasses (silica), polymers (Teflon), alloys (stainless steel) and layered combinations (carbon/ nickel, silver/sapphire) in sizes from 0.5 - 410 microns. Like many of the techniques described above, microtube technology employs a fugitive process with a sacrificial mandrel, which in this case is a fiber. High quality coating techniques very faithfully replicate the surface of the fiber on the inner wall of the coating after the fiber is removed. By a proper choice of fiber, coating, deposition method, and mandrel removal method, tubes of practically any composition can be fabricated. Obviously, to make precision tubes of high quality, a great deal of material science is involved. Some scanning electron microscope (SEM) micrographs of a group of tubes can be seen in Figure 1.

Cross-sectional shapes as well as wall thickness can be very accurately controlled to a fraction of a micron, which is not possible with any of the approaches cited above. Numerous cross-sectional shapes have already been made and some of these can be seen in Figure 2. These micrographs should be sufficient to demonstrate that practically any cross-sectional shape imagined can be fabricated. As seen in Figure 2, the wall thickness of the tubes can be held very uniform around the tube. It is also possible to accurately control the wall thickness along the length of the individual tubes as well as among the tubes in a batch or a continuous process. It can also be seen in Figure 2 that the walls can be made non-porous. It will also be shown below that the microstructure of the walls and extent of porosity that the walls contain can also be controlled. In additional to the possibility of cross-sectional tube shapes, using a fugitive process also allows the fabrication of tubes with practically any axial geometry as will be shown below.

The maximum length that these tubes can be made has yet to be determined because it depends on many variables, such as, type of tube material, composition of sacrificial tube forming material, degree of porosity in the wall, etc. It is possible that with a porous wall there is no limitation in length. For a non-porous wall the maximum length would probably be in the meter range with there being a direct relationship between the tube ID and the maximum possible length. However, for most applications conceived to date, the length need only be on the order of a few centimeters. If one does a quick calculation it is apparent that even "short" tubes have a tremendous aspect ratio. For instance, a 10-micron ID tube 1-inch long has an aspect ratio of 2500.

With microtube technology, there is no upper limitation in wall thickness with most materials. To date, free-standing tubes have been made with wall thicknesses from 0.01 microns to 800 microns (Figure 3a). Most of the microtubes tested to date have demonstrated surprising mechanical strength. In fact, preliminary studies with both copper and silver tubes with wall thicknesses in the micron range have shown that microtubes can have up to two times the tensile strength of an annealed wire of the same material with the same cross-sectional area. Besides being able to precisely control the tube wall thickness and composition, the interior surface of these tube walls can have practically any desired texture or degree of roughness. In addition, the walls can range from non-porous to extremely porous as seen in Figure 4, and the interior or exterior surface of these tubes can be coated with one or more layers of other materials (Figure 5),

In addition to free-standing microtubes, solid monolithic structures with micro-channels can be fabricated by essentially making the tube walls so thick that the space between the tubes is filled (Figure 6). The micro-channels can be randomly oriented or they can have a predetermined orientation. Any desired orientation or configuration of microtubes can be obtained by a fixturing process. Alternatively, composite materials can be made using a material different than the tube wall as a "matrix" that fills in the space between the tubes. The microtubes imbedded in these monolithic structures form oriented micro-channels which, like free-standing tubes, can contain solids, liquids and gases, as well as act as wave-guides for all types of electromagnetic energy.

Microtube applications

Discrete thinner-walled microtubes are useful in areas as diverse as spill clean-up, encapsulation of medicine or explosives, insulation that is useable over a very wide range of temperature, and as lightweight structural reinforcement similar to that found in bone or wood. The cross-sectional shape of these reinforcement tubes can be tailored to optimize mechanical or other properties. In addition, thinner-walled tubes are useful as bending or extension actuators when fabricated from smart materials. Thicker-walled tubes (Figure 3b Nickel, SS), which are just as easily fabricated, are needed in other applications, such as calibrated leaks and applications involving internal or external pressure on the tube wall.

The ability to coat the interior or exterior surface of these tubes with a layer or numerous layers of other materials not only enlarges the use environment of the microtubes but also allows the fabrication of certain devices. For example, applying oxidation or corrosion protection layers on a structural or specialty tube material will greatly enlarge its use envelope. A catalyst can be coated on the inner and/or outer tube surface to enhance chemical reactions. The catalytic activity of the tube can also be enhanced by increasing the porosity in the wall as shown above in Figure 4. With multiple alternating conductive and insulating layers on a tube, a multiple-path micro-coaxial conductor or a high density micro-capacitor will result.

As stated above, the interior surface of these tube walls can have practically any desired texture or degree of roughness. This control is highly advantageous and allows the use of microtubes in many diverse applications. For example, optical wave-guides require very smooth walls while catalytic mixing-reactors would benefit from rough walls. (Because of the fabrication technique, the roughness on the interior of the tube wall can be quantified to a fraction of a micron using scanning probe microscopy techniques on the mandrel.)

Microtubes can be made to be straight or curved (Figure 7), or they can be coiled (Figure 8). Coiled tubes with coils as small as 20 microns can be used, for example, as flexible connectors, or solenoid coils. For this later application, the coils could be of metal or of a high temperature superconductor with liquid nitrogen flowing through the tube. Another application for coils is for force or pressure measurement. No longer are we limited to quartz microsprings. With microtube technology, the diameter and wall thickness of the tube, the diameter of the coil, the tube material and the coil spacing can be very precisely controlled to give whatever spring constant is needed for the specific application. In addition, these microcoils can be made from a variety of smart materials and used as actuators or sensors. For example, a spring made from Nitinol can easily change its length by the application of heat. It is also possible to wrap one or more coiled

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spring tubes around a core tube (Figure 9). Applications for this kind of device range from a counter-flow heat exchanger to a screw drive for micro-machines. {For the screw application, the wrapped coil cross-section could be made rectangular.}

Like the coiled spring tubes, bellows can be used as micro-interconnects, sensors, and actuators and can be made in practically any shape imaginable. Figure 10a shows a bellows with circular cross-section while the bellows in Figure 10b has a square cross-section with aligned bellows segments. The bellows in Figure 10c is a square bellows with a twist. A slightly more complex bellows is shown in Figure 10d. This is a tapered-square camera bellows with a sun-shade to demonstrate the unique capability of this technology. That is, it demonstrates the ability to control cross-section and axial shape as well as to be able to decrease and increase the cross-sectional dimension in the same device. Bellows fabricated with microtube technology can have various shaped ends for connections to systems for use as, for example, finned heat exchangers, hydraulic couplings for gas and liquid, or static mixers for multiple fluids. The bellows in Figure 10e has a thicker transition region and dovetail on the end for connection to a device machined on a silicon wafer. The female dovetail to mate with this bellows is a commercially available trench design [68] on a silicon wafer and provides a way to attach the bellows to the wafer, which with proper sealing, can be pressurized. (There is no other technology available that is able to join a fluidic coupling to a wafer and pressurize it.)

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If one end of the bellows is sealed, an entirely new group of applications become possible. For example, if a bellows end is sealed, the bellows can be extended with hydraulic or pneumatic means. In this configuration, a bellows could be used as a positive displacement pump, a valve actuator, or for micro-manipulation. As a manipulator, a single bellows could be used for linear motion, three bellows could be orthogonally placed for 3D-motion, or three bellows can be attached several places externally along their axis (Figure 11) and differentially pressurized to produce a bending motion. This bending motion would produce a micro-finger and several of these fingers would make up a hand. The large forces and displacements possible with this technique far surpass those currently possible by electrostatic or piezoelectric means and fulfill the need expressed by Wise and Najafi [18] when they stated that "In the area of micro-actuators, we badly need drive mechanisms capable of producing high force and high displacement simultaneously."

For most applications it is necessary to be able to interface microtubes with the macro-world. This is possible to achieve in a number of ways. For example, a tapering process can be used in which the diameter is gradually decreased to micron dimensions. Alternatively, the tubes can be interfaced to the macro-world by telescoping or through numerous types of manifolding schemes (Figure 12). An example of a thin-walled 5- don't break micron I.D. tube telescoped to a 250-micron O.D. tube can be seen in Figure 13. A tube of this type could be used as a micro-pitot tube and, of course, could be made more robust by thickening the walls.

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Although microtube technology has unique capabilities, it should be obvious that no single technology can fill all the requirements imposed by diverse applications. Thus, microtube technology can not easily compete with other technologies in certain applications. One of these involves gas and liquid separation such as chromatography.

For example, quartz tubing, which can be extruded and drawn in very long lengths, is inexpensive and available in micron dimensions. However, it should be noted that even in areas such as separation, there are niches for microtubes that involve the composition of the tube material, the cross-sectional shape, or the inner wall coating. For example, Figure 14 shows microtubes manifolded to a tubular frame for a specific gas separation application that requires microtubes of a specific composition with precise diameter and wall thickness.

Currently, these tubes have been made by a batch process in the laboratory, but the technique is equally suited to a continuous process which would not only be more efficient but in some cases much easier. Obviously, a continuous process would reduce costs. For most materials these are already rather low because, unlike some other processes, expensive tooling is not required. For many materials such as quartz, aluminum, copper, etc. the cost is anticipated to be ~ \$0.01/cm for thin-walled tubes. For precious metals such as gold or platinum, the cost would be significantly higher due to the cost of raw materials.

Microtubes appear to have almost universal application in areas as diverse as optics, electronics, medical technology, and micro-electromechanical devices. Specific applications for microtubes are as diverse as chromatography, encapsulation, cross- and counter-flow heat exchange, injectors, micro-pipettes, dies, composite reinforcement, detectors, micropore filters, hollow insulation, displays, sensors, optical wave guides, flow control, pinpoint lubrication, micro-sponges, heat pipes, microprobes, plumbing for micromotors and refrigerators, etc. The technology works equally well for high and low temperature materials and appears feasible for all applications that have been conceived to date. As can be seen, there are numerous types of devices that have become possible as a result of microtube technology. One category of devices that will be highlighted is those based on surface tension and wettability.

MICROTUBE DEVICES BASED ON SURFACE TENSION AND WETTABILITY

At the present time there is great interest in developing micro-fluidic systems to decrease the size of current devices, increase their speed and efficiency, as well as to decrease their cost. This is because micro-fluidic systems have the potential, for example, of drastically decreasing the cost of certain health tests, allowing implantable drug delivery systems, and very significantly reducing the time needed to complete the Humane Genome Project. Microtube technology based on surface tension and wettability is unique in its capabilities and is truly an enabling technology in the microfluidic field.

Reference this.

As miniaturization of mechanical, electrical, and fluidic systems occurs, the role of physical and chemical effects and parameters ~~have~~ has to be reappraised. Some effects, such as those due to gravity or ambient atmospheric pressure, are relegated to minor roles, or can even be disregarded entirely as miniaturization progresses. Meanwhile, other effects become elevated in importance or, in some cases, actually become the dominating variables. This "downsizing reappraisal" is vital to successful miniaturization. In a very real manner of speaking, new worlds are entered into, in which design considerations and forces that are normally negligible in real-world applications become essential to successful utilization and application of the miniaturized technology.

Some of your paragraphs are justified / others aren't

Surface tension and wettability are closely related phenomena that are greatly elevated in importance as miniaturization proceeds. While surface tension only involves the strength of attraction of droplet molecules for one another (cohesive forces), wettability also includes the strength of attraction of droplet molecules with molecules of the wall material (adhesive forces). It is important to realize that surface tension and wettability are usually not comparable in effect to normal physical forces at macroscopic levels. For example, surface tension is usually ignored when determining fluid flow through a pump or tube because its effect is many orders of magnitude smaller than pressure drop caused by viscosity. That is because the difference in pressure, ΔP, existing between the inside of a droplet and the outside is given by the Young and Laplace equation of capillary pressure (69-70)

$$\Delta P = 2\gamma / r \qquad (1)$$

In this equal-radii form of the capillary pressure law used for a spherical droplet, γ is surface tension and r is droplet radius. This pressure inside the droplet can be thought of as being caused by a surface "skin", similar to a balloon holding in air. Instead of a thin membrane of rubber as in the case of balloons, however, confining forces in surface tension are caused by the affinity of molecules of droplet material for one another. On the surface of a drop, because molecules are missing a binding partner looking outward, they pull on their nearest neighbors.

Normally, in most macroscopic applications, droplet dimensions are measured in thousands of microns. Pressure differences due to surface-tension effects are therefore inconsequential, typically measuring far less than atmospheric pressure. For comparison, pressure drops resulting from viscous flow are typically on the order-of-magnitude of tens-of-atmospheres. When r is on the order of microns, however, pressure differences due to surface tension become enormous, frequently surpassing hundreds of atmospheres. This is precisely the reason why fine aerosol droplets are so difficult to form. However, it is not specifically formation of tiny droplets that is the focus of discussion here, but rather their behavior in miniature voids, such as cavities, capillaries, and channels that are shaped in such a fashion so as to be partially confining to the droplet. The position of droplets within such micro-voids is governed by the surface tension of the droplet fluid, the wettability of the fluid with respect to micro-void walls contacted during displacement, the geometric configuration of the walls confining the fluid droplets, and any pressure external to the droplet. Micro-devices fabricated using these micro-voids can be made to operate with wettabilities greater than or less than ~~ninety degrees~~ 90°, but not exactly ~~ninety degrees~~ 90°. That is, with either non-wetting of wetting fluids. The difference between wetting and non-wetting fluids in capillaries can be explained using Figure 15.

consistency - see pg. 25

not a sentence

In Figure 15a, a non-wetting fluid droplet is forced into a single microtube. An insertion pressure has to be employed to push the non-wetting droplet inside the microtube because there is a repulsion between the droplet and the walls. Once it is inside, however, no further pressure is necessary. In fact, any pressure will simply move the non-wetting droplet along the microtube with a velocity determined by the applied pressure as well as the frictional forces between the droplet and the microtube wall. It should be noted that the non-wetting droplet becomes elongated when it is constrained in the capillary and has a convex shaped interface along the axis of the capillary. In addition, it can be seen that the radius of the non-wetting droplet is now the radius of the micro-device tube and that the contact angle with the capillary surface , θ, is between 90° and 180°, which is the contact angle for totally non-wetting droplet. In contrast, the situation is very different if the fluid totally wets the microtube surface as seen in Figure 15b. In this case the fluid will be sucked into the microtube and fluid flow will governed only by frictional forces. This is the situation in normal macroscopic applications. With wetting fluids, the ends of the droplets are now concave because the walls of the micro-device are now wet by the droplet and attract the droplet molecules. The contact angle for wetting fluids is between 0° and 90°, with zero degrees being a totally wetting fluid. In this manuscript, the term non-wetting will refer to a contact angle greater than 90° and the term wetting will mean a contact angle less than 90°.

The behavior of microtube devices employing non-wetting droplets is easily understood if one compares it to the mercury intrusion method (71-73) of measuring the pore-size distribution within porous solids. This technique is based on the understanding that the pressure needed to force a non-wetting fluid into a capillary, or pore in a solid, is given by the relationship proposed by Washburn (71):

$$P = 2\gamma\cos\theta/r \qquad (2)$$

where θ is the contact angle of the fluid with the material under test, P is the external pressure applied to the non-wetting fluid, and r is the radius of the capillary or pore which is assumed for simplicity to be spherical with a constant diameter. This equation is valid for any fluid in contact with a capillary or porous solid having a contact angle greater than 90° ~~ninety degrees~~. Once the external applied pressure exceeds that needed to insert the non-wetting fluid into a constant-diameter capillary or pore, the non-wetting fluid will flow into that particular diameter capillary or pore until it fills it. The volume of the intruded fluid is then a direct measure of that particular capillary's or pore's void volume. If a smaller capillary or pore branches off the larger-diameter void, it will remain unfilled until the insertion pressure is raised sufficiently high that Equation 2 is again satisfied, and the process repeats itself.

In contrast to the mercury intrusion method of determining pore volume, instead of determining the pore volume, the emphasis in devices based on microtube technology is placed on the movement and the position of the droplet in the confining voids. These droplets can be wetting or non-wetting. As will be apparent below, there is ~~are~~ a myriad of smart micro-devices that are based on surface tension and wettability.

Because these micro-devices have no moving mechanical parts, they are very reliable, are able to be used in both static as well as dynamic applications, and are very rugged. That is, they can experience pressures or forces far beyond their normal operating range and still return back to their original accuracy and precision. In addition, unlike technology built up on a silicon wafer, these microdevices can be made from practically any material. Thus with the proper choice of device and droplet material, high temperature microdevices can be fabricated.

you indented sub-heads before

Devices utilizing the interaction of non-wetting droplets with gases and wetting fluids

This group of devices utilizes the surface properties of materials, primarily surface tension and wettability, as the principle means of actuating and controlling motion both by and within microtube devices. These devices, which have no moving mechanical parts, are capable of performing mechanical tasks whose scale of motion is measured in microns.

These devices, similar to other micro-devices based on surface tension and wettability, are composed of various sizes of non-wetting droplets inserted into microscopic voids of various shapes and sizes. These voids can be in the form of cavities, capillaries, and channels that are shaped in such a fashion so as to be partially confining to the droplet. Gas or wetting fluid is placed in the micro-cavities along with the non-wetting fluid. During operation the non-wetting droplets move in response to fluid or gas pressure or vice versa. Specifically, these non-wetting droplets may translate within a void of the microtube device which is filled with the gas or wetting fluid, translate from one void space to another, or rotate in a fixed positions. Microtube devices of this type are able to stop fluid flow or act as a check-valve, a flow restrictor, a flow regulator, or a gate, for example. The minimum dimension of the voids in these devices typically range from about 20 nanometers to about 1000 microns.

In Figure 16~~A~~a, a non-wetting fluid droplet is forced through a single microtube. An initial insertion pressure has to be employed to push the non-wetting droplet inside the microtube. If the diameter of the microtube in Figure 16~~A~~a is decreased at a certain point forming a telescoping microtube, (Figure 16~~B~~b), a considerably higher pressure must be applied by a gas or wetting fluid to squeeze the non-wetting drop into the smaller section of the microtube. In contrast, if a wetting fluid is employed instead of a gas, as was the case above, it will also be sucked into the smaller diameter section, completely filling all the available space in the micro-cavity. By inserting an appropriately ~~-~~sized non-wetting droplet into a tapered microtube or a microtube with a transition to a smaller dimension that is filled with a second fluid that wets the tube walls, all flow of the wetting fluid can be stopped by applying a pressure that forces the non-wetting droplet to block the entrance to the smaller section of the cavity. This is the situation in Figure 16~~B~~b where the non-wetting droplet has been forced to the intersection of the larger and smaller microtube sections by the flowing gas or wetting fluid. Figures 17~~A~~a and 17~~B~~b illustrate an extension of this concept. By adding additional small-diameter bypass-flow paths to one end of a doubly constricted tube, flow will only be possible in the direction of the end having the added flow paths attached to the cavity. Of course, these bypass tubes must be properly sized to prevent non-wetting droplets from squeezing into them. This microtube device in Figure 17 acts as a check-valve with no solid moving parts which simply cannot be achieved at the macroscopic level because forces arising from surface tensions of fluids are too small due to the much larger geometries employed.

Figures 18 and 19 are further extensions of this same concept. In Figure 18, bypass tubes are left off the microtube check-valve converting it to either a microtube flow-limiter (Figure 18) or a microtube flow-restricter (Figure 19). In Figure 18, since the non-wetting droplet forms a seal with the larger tube wall, the only wetting fluid flow that can now occur in either direction when the non-wetting droplet travels back and forth is equal to the volume of the larger tube section minus the volume of the non-wetting droplet. In Figure 19, the diameter of the non-wetting droplet is now smaller than the diameter of the larger microtube section, but larger than the diameter of the smaller microtube. Thus, flow can now take place around the non-wetting droplet. However, fluid flow is not merely restricted, but will be entirely stopped with enough flow to push the drop to one end blocking the smaller tube.

Figure 20 illustrate a microtube flow-regulator. In this device bypass tubes have openings or are open along their entire length to a conically-shaped transition region placed in-between the larger and smaller diameter tubes. Furthermore, the length of the joined-bypass tubes (now better described as bypass channels) up to the conical transition region can be varied. Increased pressure forces the non-wetting droplet further into the conical transition region exposing more flow channel openings to wetting-fluid. The result is increased flow of the gas or wetting fluid as a function of pressure. By suitable sizing the non-wetting droplet, correctly shaping the transition cone, and precisely positioning bypass channels, this device can function as a microtube pressure-relief valve; i.e., no flow occurs until some predetermined pressure is exceeded. Flow then takes place as long as pressure is maintained. It should be noted that only two bypass-flow channels are shown in Figures 20. This was done to simplify drawing. Any convenient number, one or more, of channels can be employed. Finally, by making bypass-flow channels vary in cross-sectional area, uniformly increasing or decreasing flow can be made to occur as a function of pressure.

In addition to a check valve, it is possible to use non-wetting fluids to make a positive closure valve with zero dead space to control a gas or wetting fluid. Figures 21~~A~~a and 21~~B~~b illustrate a microvalve composed of a fill tube joined to an end bulb, with two microchannels being attached to the fill tube. In this example, it is the non-wetting droplet that controls the flow of a wetting fluid or gas through a microchannel with a thickness less than that of the fill tube. In this microvalve an inlet fluid flows through an inlet duct and then into one of the microchannels. If the fill tube is not blocked by the non-wetting droplet, the inlet fluid traverses the unblocked fill tube at the point where both microchannels attach to it. The fluid then exits the microvalve through an outlet duct as outlet fluid. In Figures 21~~A~~a and 21~~B~~b, the non-wetting droplet is activated by a heater, and only partially fills the fill tube. Obviously, many other forms of activation are possible and it is possible to assemble these microvalves together in parallel to control large flows of liquids or gases.

A final category of microfluidic devices in which one fluid controls another can be understood by the more complex examples given in Figures 22~~A~~a and 22~~B~~b. These figures present microtube devices utilizing surface tension and wettability, in fluidic logic circuits that are fully digital, not analog, in nature. The device in Figure 22~~A~~a obeys the NOR algorithm; i.e, if pressure is applied to either branch A or B, the gate (non-wetting droplet #2) will close as in Figure 22~~B~~b and no flow will occur (and no pressure will be transmitted) between branches C and D. If equal pressure is applied to A and B, or no pressure is applied to A and B, the gate will remain open as in Figure 22~~A~~a and flow (and pressure) will be transmitted~~)~~ between C and D. The non-wetting droplet #1 is returned to center position whenever pressure is removed because surface tension always minimizes droplet surface area, and a sphere has the lowest surface area per unit volume of any object. Only at the center position can it be a sphere, and unless placed under unbalanced force by pressure from A or B, it will remain at center. Numerous other types of logic circuits, such as OR and AND gates, are also capable of being fabricated in this manner but will not be presented. By combining a number of these logic components together in a suitable arrangement, digital operations can be performed in a manner identical to electrical devices. Instead of electricity either being on or off in a circuit, pressure would be applied or not applied, and fluid flow would or would not occur.

<u>Micro-devices based on the position and shape of non-wetting droplets</u>

In this group of micro-devices the basic principle of operation is the movement or shape change of non-wetting droplets in tubes, channels, or voids with at least one microscopic dimension, as a result of either external or internal stimuli. The change in droplet shape will depend on the cavity shape~~,~~ and will always be in a manner that results in a minimization of the surface free energy of the droplet. The cavity which constrains the droplet in these devices can be sealed or have one or more openings. It is the shape of this cavity that determines the reaction of the droplet to a stimulus as well as the use of the microdevice and the output that can be obtained from it. Uses for these microdevices are as diverse as sensors, detectors, shutters, and valves.

As just stated microtube sensors based on surface tension and wettability are one type of device in this group. Some of these sensors respond to one or more external stimuli such as pressure, temperature, and gravity or acceleration by changes in the displacement or shape of liquid interfaces contained within microtubes and/or microchannels, which have either fixed or variable axial geometries as well as circular or noncircular cross-sectional profiles. Other sensors respond to internal stimuli, such as a change in surface tension of the liquid droplet or a change in the wettability of the microdevice's internal walls. Some of these sensors are able to quantify the displacement or change in shape of the constrained droplet that is a result of external or internal forces acting upon it.

An example of one of the simplest microdevices in this group of devices~~,~~ is a microtube pressure sensor (Figure 23) using a non-wetting fluid in the form of a droplet. Figure 23~~A~~a illustrates the position of the droplet when the entrance pressure, P_{ent} is equal to the device pressure, P_{dev} . Figure 23~~B~~b illustrates the position of the droplet when the entrance pressure is greater than the device pressure, P_{dev}. ~~While~~ figure 23~~C~~c illustrates the position of the droplet when there is a much higher entrance pressure. This sensor demonstrates the reaction of such a device to an outside stimulus which in this case is an increase in external applied pressure, P_{ent}. As can easily been seen, the shape of the non-wetting droplet changes in reaction to increases in applied external pressure, P_{ent}. More precisely, increasing the external pressure, P_{ent}, acting through an entrance microtube, squeezes the droplet into ever-smaller-diameter locations within a microcavity, which results in displacement of the non-wetting interface towards the smaller-diameter end of the device. For this type of sensor this microcavity may be teardrop shaped, circular in shape~~d~~, or have practically any shape as long as there is a change in at least one dimension and this dimension is between 0.003 and 1000 microns. For purposes of simplicity, the pressure on the smaller side of the microdevice, P_{dev}, which opposes the external pressure, P_{ent}, is set at zero in this figure. P_{dev} is perhaps most easily thought of as a residual gas pressure left over inside the device from the actual fabrication process. It does not have to be zero as will be shown later. The only real requirement for this type of sensor is that P_{dev} be less than P_{ent}, and that both pressures be smaller than the bursting strength of the walls of the microtube pressure sensor. It should be apparent from Figure 23 that an over-pressure of the device will push the droplet further into the device tube than was designed, but when the pressure is released, the droplet will return to its equilibrium position. As long as the walls of the device have not been damaged and maintain their original shape, the sensitivity and accuracy of this device and the others that will be described below will be unaffected by the over-pressure event.

While the reaction of the droplet to external pressure is easily calculable from surface-tension theory (the change in radius of the smaller-end of the droplet is inversely proportional to external applied pressure), the actual decrease in radius and resulting displacement of the non-wetting interface can only either be understood intuitively or observed visually with a microscope, as presented in Figure 23. Figure 24 illustrates a modification to this microtube pressure sensor based on surface-tension/wettability which enables non-visual determination of the displaced interface. This non-visual response to the reaction (movement or shape change) of the droplet interface caused by a stimuli can take many forms. One of these is a change in electrical resistance. A center contact which has a measurable electrical resistance is inserted through the microtube device, establishing electrical contact with the non-wetting droplet. This center contact can be a wire, tube, tape or any other elongated geometry desired. A second or side contact is likewise placed in such a position so as to also make electrical contact with the conductive droplet, but not make direct contact with the center contact. These two contacts are then connected to an apparatus which measures resistance. If the non-wetting droplet material composition has been selected in such a fashion so as to be electrically conductive as well as non-wetting, any displacement of the non-wetting interface which reduces the length of the center contact not touching the droplet thereby results in a reduction of the center contact's resistance as measured by the resistance measuring apparatus. To maximize this effect, the center contact should have a very high resistance per unit length compared to the side contact, the actual droplet itself, as well as compared to the remainder of the circuit connecting both contacts to the resistance-measuring apparatus.

As stated previously the opposing pressure, P_{dev}, need not be zero. It has been set at zero thus far for simplicity. For this type of sensor it merely needs to be less than the externally applied pressure P_{ent}, otherwise the non-wetting droplet could be expelled from the microtube pressure sensor.

It should be noted here that the devices shown schematically are able to measure a variety of external or internal stimuli. That is, the pressure sensor in Figure 24, for example, could also measure acceleration and oscillation along the device axis as well as rotation and temperature, which affects both the thermal expansion and the surface tension of the droplet. In fact, if another center contact is also placed in the device on the end opposite the present center contact, the device can measure acceleration in two directions. In addition, it should be apparent that to measure parameters such as temperature, rotation, acceleration or oscillation it is not even necessary to have the entrance tube and the device tube open to the atmosphere. Thus, to measure these external stimuli or some internal stimuli, a totally sealed cavity would function as well as the open pressure sensor in Figure 24.

For purposes of simplicity, only pressure sensors will be shown schematically and it should be understood that the devices work equally well in reaction to many other stimuli. A partial list, which includes: vibration, acceleration, rotation, temperature, electromagnetic fields, and ionizing radiation, demonstrates the broad scope of this sensor technology.

When a wetting droplet is employed in place of a non-wetting droplet, instead of needing P_{ent} to reach some value given by equation 2 in order to force the droplet into the microtube, it goes in automatically. This behavior is often referred to as "wicking." In contrast to the non-wetting droplet situation, no pressure is needed to get the drop into the tube, but a pressure identical to that needed to force the non-wetting droplet in, but which acts in the reverse direction, is needed to force the wetting droplet out of the tube.

This would be provided by P_{dev}. The fact that wetting droplets behave similarly to non-wetting droplets in some respects means that microdevice sensors can employ either wetting or non-wetting fluids as the droplet material, and still serve the same function. In the case of microtube pressure sensors, this would require modifying ~~which~~ the side of the droplet which actually "feels" the applied pressure. Microdevices sensing other stimuli would also need similar kinds of modification. These would be specific to the actual sensing application.

Figures 25~~A~~a and 25~~B~~b illustrate the relationship between the radius of curvature of the small end of the drop r_{dev} and the various pressures involved for a microtube pressure sensor ~~which~~ that has a digital type of response, which will hereafter be referred to as a "Yes-No" response. In Figure 25~~A~~a, the applied pressure P_{ent} is not sufficient, compared to P_{dev}, to force the non-wetting droplet into the straight port. The continuity apparatus therefore registers an open circuit, or "No" response. In Figure 25~~B~~b, the applied pressure, P_{ent}, is sufficient to force entry of the non-wetting droplet into the straight port. Once the droplet has entered the straight port, it completely fills it and the continuity apparatus registers a closed circuit, or "Yes" response. As mentioned previously, this same kind of "Yes-No" response can be duplicated using wetting fluids. However, since a wetting fluid would spontaneously wick into the smaller diameter tube, the only difference would be that now an applied pressure of sufficient magnitude would need to be directed to P_{dev} in order to expel the wetting droplet from that same straight tube. For a wetting fluid the continuity apparatus would therefore work in reverse to the "Yes-No" response for a non-wetting droplet. In this case, P_{dev} must be greater than P_{ent}

and therefore an open circuit signifies "Yes" and a closed circuit signifies "No." However, because a wetting droplet adheres to the microdevice walls, including the straight port, fluid remaining on these surfaces might compromise the accuracy of the continuity apparatus. It is therefore preferable to use non-wetting droplets in this kind of sensor. This same logic applies to most microdevices based on surface tension and wettability, and so in the discussion that follows only non-wetting behavior will be illustrated.

There are obviously many other means to measure displacement of the non-wetting droplet. Other basic electrical parameters which can be employed are capacitance and inductance. It should be noted here that with all the aforementioned techniques for measuring displacement of the non-wetting droplet using electrical means, the electrical properties of the non-wetting droplet must, of course, be suitable for the measurement technique employed. For some applications, the resistance of the non-wetting droplet must be sufficiently low to permit resistivity measurements of the center contact to be made accurately enough for the application at hand. For other applications the conductivity must be high enough to enable capacitance to be accurately measured. For certain applications, permeability must be sufficiently different between the non-wetting droplet and its surrounding medium in the microdevice to allow inductance to be measured accurately enough to satisfy demands of the desired application. These electrical properties requirements will most likely be different depending on the measuring technique employed and the particular application being developed. It should be noted that it is also possible to combine two or more readout techniques in a single device.

For either multi-range or redundancy-driven applications, there is a great deal of variation possible. These variations are in the form of identical or different devices, cavity, and/or channel or tube configurations as well as identical or different types of readout. It should be mentioned that many different types of device channel or tube configurations are possible that will give either linear or non-linear responses as well as analog or digital responses to the stimuli being sensed. For example, a gradual taper would produce a linear response while a very rapid taper would give a non-linear response. In another example, a device such as that shown in Figure 25 could be modified with a tapered section to follow the constant dimension tube. This would result in a digital response followed by an analog response. In addition to these differences in individual sensors, multiple sensors could all be used together at the same time, or switched on or off as needed.

As mentioned previously, the presence or absence of non-wetting material in a straight tube, Figure 25, enables the pressure sensor, or other microdevice deriving its capabilities from surface properties of materials, to function in a digital or a "Yes-No" mode of response. Figure 26 illustrates another very simple kind of "Yes-No" readout response for a pressure sensor that does not have a straight tube. The center contact in Figure 24 has now been truncated so that it does not make contact with the non-wetting droplet for low values of pressure difference between P_{ent} and P_{dev}. This lack of contact, or gap, is shown in Figure 26. The truncated center contact only makes contact with the non-wetting droplet once a predetermined pressure difference exists (P_{ent} greater than P_{dev}). Once this occurs, the continuity meter signals contact has been made providing the desired "Yes-No" readout response. Once sufficient pressure difference has been established, the truncated center contact can then function as a center resistance contact, center contact, some other kind of readout implement, or some combination thereof. The truncated center contact should not move relative to the microdevice walls in this simple form of "Yes-No" readout microdevice. It should be apparent that devices of this type with a truncated center contact can also serve as an electrical switch based on surface tension and wettability that can be made to operate independent of gravity, be impervious to radiation, and can be activated by numerous stimuli.

A more sophisticated "Yes-No" readout microdevice pressure sensor is illustrated in Figure 27. Now the truncated center contact is attached to a positioner which, in turn, is attached to a positioner holder which is itself held firmly in place relative to the actual microdevice walls. In Figure 27, the positioner holder is shown attached to the microdevice walls. The positioner is any type of device capable of moving the truncated center contact relative to the microdevice walls in a predetermined fashion. Examples of such positioning devices are numerous. They can be of the type where the operator sets the gap and thereby controls the devices' sensitivity, such as pressurized microbellows and piezoelectric crystals. Alternatively, the positioning device can be of the type which is influenced by its environment, such as those made from a photostrictive, chemostrictive, electrostrictive, or magnetostrictive materials, which change length due to light, in a chemical environment, or in an electric or magnetic field. With these types of materials, the positioner can be controlled in real time by its environment, and thus the device is able to respond to two stimuli simultaneously. Moreover, with any such positioning devices, the gap can be changed by a feedback circuit. By altering the size of the gap either before or during actual operation of the microdevice, the amount of pressure difference needed between P_{ent} and P_{dev} to establish contact and thereby evoke the "Yes-No" readout response or continuity as measured by the continuity apparatus, can be changed. Thus, the sensitivity of this device can be changed by an operator, by its environment, or a feedback circuit. As before, with the simple "Yes-No" readout response microdevice of Figure 26, once continuity has been established, the truncated center contact can be used for other kinds of readout purposes. For example, the continuity apparatus can be modified to function as the resistance-measuring apparatus shown in Figure 24. If this is done, both digital and analog readout responses can be garnered from the same sensor. Also, more than one center contact of different lengths and/or more than one side contact can be employed in Figure 26, thereby providing multiple digital responses from one device.

It should be noted at this point that the sensing techniques mentioned thus far have all been relatively simple in that they have employed principles of physics that are intuitively easy to understand; i.e., changes in resistance, capacitance, or inductance. Another simple technique to detect the position of a droplet interface is to use an electromagnetic beam impinging on a detector that is blocked by the advancing surface of the droplet. This type of arrangement can basically only give a "yes"-"no" response. Two other techniques which can also be employed to monitor displacement of the non-wetting droplet interface are optical interference and electron tunneling. These techniques are capable of much higher levels of resolution of the non-wetting droplets' displacement, which results in greater levels of sensitivity.

Figure 28 illustrates the readout technique which employs optical interference. The only additional requirement that must be imposed in order to use this technique is that the non-wetting droplet needs to be able to reflect at least some of the electromagnetic radiation input through the fiber-optics input/output cable back out through the same cable. If these conditions are met, an interference pattern can then be generated between the incoming and outgoing rays of radiation that can be detected by a suitable apparatus located at the opposite end of the fiber-optics input/output cable. This interference pattern will be highly dependent on the position of the internal interface of the non-wetting droplet, as well as on the wavelength of radiation employed. It is therefore an extremely accurate technique for monitoring any displacement of that interface.

Figure 29 illustrates the readout technique for electron tunneling. The primary difference between this readout technique and the previous readout technique employing a truncated center contact illustrated in Figure 11, is that in this apparatus the truncated center contact is replaced with a very sharp needle-shaped electrode, and the continuity apparatus is replaced with a much more sensitive electron tunneling-current detector which can measure the tiny electrical currents generated when the needle-shaped electrode moves very close to the internal interface creating gaps on the order of atomic dimensions. As with optical interference, tunneling current measurements are many

sentence very long

times more sensitive to displacements of the internal interface than simpler readout techniques discussed initially. Obviously, any other detecting technique used in scanning probe microscopy, such as atomic force, magnetic force, capacitance, etc. can be used in place of the needle-shaped electrode and the current-detection circuit. In addition the sensitivity of these devices, as with the device in Figure 27, can be changed by varying the gap between the tip and the droplet.

At this point, it is well worth mentioning again that it is the movement of a droplet in a microscopic tube, channel, or void and the process of remote measurement of displacements of the internal interface itself that is of critical significance to the devices shown, not the actual kind of remote measurement technique employed. Whatever technique is employed affects only the accuracy of remote readout. Thus, regardless of the measurement technique displacements of the internal interface in reaction to external stimulus will be the same, depending only on surface tension and wettability of the sensor components and on sensor geometry.

Up until this point, it has been tacitly assumed that motion of the internal interface during any remote readout of its displacement is negligible. This does not necessarily have to be the case. Any measurement of position of the internal interface will take some finite amount of time. If there is motion of the internal interface during this finite measurement time, some sort of average readout of position of the internal interface will occur. If this is acceptable to the designer of the microdevice, all is well. If it is not, some change in either the method of remote readout, or the level of precision of the actual analytical instruments employed must be undertaken to increase the speed of readout to the degree required. Once this has been done, microdevices based on surface tension and wettability with remote readout capabilities can function as either static or dynamic analytical detectors or sensors.

Up until this point, it has been tacitly assumed that the shaped or tapered microtubes or microchannels within which droplets move or flow under the influence of surface tension and wettability, and some external forcing agent such as pressure or acceleration, have been circular in cross-section. This does not have to be the case. Figures 30~~A~~a and 30~~B~~b illustrate flow of an elongated non-wetting droplet constrained on four sides by walls that form a square cross-section. As stated above, there will always be open corners in this kind of non-wetting flow situation when the contact angle is greater than 135° because infinite internal pressure would be required in the non-wetting droplet, the result of setting r equal to zero in the relationship given in Equation 2 in order to completely fill in all corners. This can never be true for two reasons. First, there is no such entity as infinitely-high pressure. Second, in Figures 30~~A~~a and 30~~B~~b, bypass flow of externally applied pressure P_{ent} will occur through all open corners, thereby reducing actual pressure applied to the non-wetting droplet. An analogous situation occurs when a child shoots an irregularly-shaped pea out through a circular straw. Even though gaps equivalent to the open corners in Figures 30~~A~~a and 30~~B~~b exist around the pea, the child can still expel the pea from the straw simply by blowing hard enough, thereby producing a sufficiently effective pressure on the pea to accomplish the purpose. This is exactly the situation that exists for flow of non-wetting droplets in non-circular microtubes or microchannels. Therefore all previous arguments made for remote sensing of droplet interfaces in circular cross-sectioned microtubes or microchannels apply equally well to remote sensing of droplet interfaces in microtubes, microchannels, or voids having any type of non-circular profile. Moreover, non-circular microtubes or microchannels can certainly be used in conjunction with circular microtubes or microchannels in the same microdevice. In fact, there is very good reason to do so. Non-circular microtubes or microchannels can be fabricated relatively easily using techniques such as photolithography and LIGA on a surface. This is currently done on silicon wafers by a sequence of deposition and/or etching techniques in a number of different ways, two of which will be given. A non-circular channel can be formed, for example, by etching the channel in the surface and then covering the channel by sealing a glass plate over it. Alternatively, for example, the non-circular channel can be formed by etching a channel in the surface and then filling it with a sacrificial material. Another material is then deposited over the filled channel and then the sacrificial material is removed leaving a microchannel. However, no matter how the non-circular channel is formed in the surface, bypass flow of gases occurs through the open corners they possess as illustrated in Figure 30~~B~~b. As just mentioned, this makes it difficult to apply pressure accurately and reproducibly to some non-wetting droplets contained within such microtubes or microchannels. This is not true for circular microtubes or microchannels. Thus, the presence of small circular microtubes or microchannels at appropriate positions in any device fabricated with non-circular microtubes or microchannels will allow either gases or wetting fluids to apply hydrostatic pressure to microdevices containing non-wetting droplets with an efficiency of 1. The reverse is also true. The presence of a circular cross-section in the device will also allow the non-wetting droplet to apply force to the gas or wetting fluid with an efficiency of 1. This also means it is possible to have wetting and non-wetting fluids present in the same microdevice. Finally, it should be stated that regardless of the cross-sectional shape of the microtubes, microchannels, or voids, all wetting fluids will have an efficiency of 1.

It is extremely important to realize that the previous discussion also illustrates that the elongated non-wetting droplet confined within a microtube or microchannel having, for the sake of illustration, square walls can serve purposes other than remote sensing. For example, it can be used to act as a shutter in optical applications, with the presence or absence of the droplet controlling whether or not light or other electromagnetic radiation is allowed to pass through the square microchannel walls. In this instance, the non-wetting droplets ~~functions~~ function in much the same fashion as a window blind does, controlling whether or not light is let through a window depending on whether or not the blind is up or down. It could also control particle beams in a similar manner.

Figure 31 illustrates a much more familiar-looking shutter mechanism that could very easily function in a fashion identical to traditional mechanical shutters. An end bulb is connected to a fill tube, and both are filled with a non-wetting liquid, which is called the working fluid and is opaque for the particular application. A rectangular void is also connected to the fill tube, but has a thickness less than the diameter of the fill tube. (The thickness of the void in this figure is exaggerated for clarity.) The shutter with constant void thickness is illustrated in the open configuration in Figures 31~~A~~a and 31~~B~~b with the incident radiation or particle beam passing through the shutter, and closed in Figures 31~~C~~c and 31~~D~~d with the incident beam or radiation blocked by the shutter. The void width and void length can be much greater than the void thickness and, in fact, only one void dimension has to be macroscopic in order to carry out a shutter's intended function in the normal macroscopic world. This illustrates an extremely important point. That is, although all the dimensions of a device can be microscopic, only one dimension of a device needs to be in the range where surface tension and wettability become dominate factors in the device's reaction to internal or external stimuli for the device to be considered a microdevice. The rectangular shutter with constant void thickness illustrated in Figures 31~~A~~a and 31~~B~~b must be considered a microdevice because of the microscopic dimensions of its thickness, even though it can have very macroscopic dimensions for one or more of its other features. This is true for all micro-devices based on surface tension and wettability. In this example, the method of actuation of the rectangular shutter shown in Figure 31 is derived by an externally~~-~~generated electrical current input through a heater contained within the working fluid. As the working fluid expands due to this heat input, any gas bubbles or other gas filled voids contained within the working fluid become compressed, thereby raising the internal pressure, P_{int}, within the working fluid. This thrusts the internal interface farther and farther into the rectangular void. At some point, the radius will decrease sufficiently so that the internal interface will shoot across the void length providing the volume of compressed gas-filled voids is much larger than the volume of the shutter. This will close the shutter in the same fashion as the "Y~~ES~~-N~~O~~" devices described earlier in Figure 25. If gas bubbles or other gas filled voids are not present in the working fluid, then the heat input will not

earlier these were upper/lower case / consistency cause a "YES-NO" type of reaction, but rather will enable the shutter to close in a more gradual fashion. In this way a partially closed shutter can be maintained by appropriately controlling the heat input. The gradual closing capability can be obtained with pressure-activated shutters by employing a void thickness that has a decreasing taper. A different tapered end is shown at the end of the rectangular void where the working fluid stops in the closed position. This is to minimize water-hammer effects and does not have to be present for the shutter to work as intended. Of course, external pressure or some other external stimuli as well as an internal stimuli could also be used in place of the heater and the shutter would still function. If pressure were employed, it would then in fact be a pressure sensor with some macroscopic dimensions that would be very easy to observe. That is, the filling of the void would signify that a certain pressure had been reached. Obviously there are numerous other applications of this technology but only two others will be mentioned. One involves using a reflective non-wetting fluid so that a mirror results when the void space is filled and the second application encompasses a much larger microscopic void area. That is, if the void space is made as large in area as a window pane, solar energy acting on the reservoir could be used to force liquid into a void of microscopic dimensions in the window pane and thus block sunlight from going through the window if an opaque non-wetting liquid is employed.

The void shown in Figure 31 is of constant thickness and is rectangular. Neither parameter is necessary. Figure 32 illustrates a circular shutter, which has a straight top face and a curved bottom face making up the void. Now, depending on the amount of expansion of the working fluid caused by electric power supplied to the heater, the shutter can be completely open with the working fluid all contained within the outside bulb, completely shut with no circular gap in the center at all, or anywhere in between as Figure 32 illustrates. Certainly, both the top face and bottom face can be curved or straight, and virtually any shutter geometry can be employed. Likewise, actuating techniques other than heat input to the working fluid by an internal heater can be used. External heat input by radiation or conduction, or changes in the internal pressure of the working fluid by any other means can be used to achieve the same resulting shutter behavior.

As mentioned earlier, surface tension and wettability govern the position of droplets within microdevices. Thus, in addition to the external stimuli already mentioned, any external stimuli which changes either surface tension of the droplet or wettability of the surface can therefore be detected by a suitably designed microdevice sensor. Some, but not all, such stimuli include the following: temperature, magnetic field, electrical field, rotation, radiation, and beams of particles.

Up to this point all the microdevice sensors illustrated have been designed to respond to external stimuli. This is not the only mechanism for causing displacement of microdevice droplets. Any compositional change that occurs within droplets themselves or on the walls of microdevices can also change surface tension or wettability. These changes can be either reversible or irreversible and can be caused by a gas or wetting fluid in the device along with the non-wetting droplet. In addition, surface tension of the droplet increases with an increase in both the temperature and rotation. If these or any other internally induced change to a microdevice's surface tension or wettability occurs, it can be detected and monitored remotely using any of the techniques described previously. Obviously, these internally-induced changes to a microdevice's surface tension or wettability can also be used to move the droplet(s) to perform work.

Up until now, no actual dimensions of either microtubes or microchannels have been discussed. Assuming a non-wetting fluid such as mercury, which has a room-temperature surface tension of approximately 470 dynes/cm and a wettability on glass microdevice walls of roughly 140 degrees, one can calculate the following droplet radii for the indicated internal pressures using Laplace's equation modified to include the effect of wettability:

P_{int} in lb/in2	r_{dev} in microns
0.2	950
2.0	95
20	9.5
200	0.95
2,000	0.095
50,000	0.003

In this section, we have shown that the flow of droplets within microtubes and microchannels that is controlled by surface tension and wettability can be used to sense both qualitatively and quantitatively any environmental factor which acts on a droplet or affects either its surface tension or wettability, or both. This sensing can be performed remotely by a variety of techniques. It has also been demonstrated that wetting droplets can sometimes also be used with only minor device modifications. Static as well as dynamic remote sensing can be performed, and microtubes or microchannels having circular or non-circular cross-sections and variable axial geometries can be employed either individually or together. The reaction of these devices to any stimuli can be tailored by the device geometry and method of sensing resulting in linear and non-linear analog output as well as digital output. The use of this technique in non-sensing applications which perform mechanical functions was also demonstrated. Finally, whenever at least one microdevice dimension lies between 1000 microns and 0.003 microns, it has been shown to be capable of performing all the various tasks that have been discussed.

Non-wetting droplets performing work.

The preceding discussion has indicated that the movement of non-wetting droplets within microtubes or microchannels can be used for sensing and the control of fluids. In addition, microscopic non-wetting droplets can be used for mechanical control and manipulation within microdevices including tasks such as position control, moving objects, deforming objects, pumping fluids, circulating fluids, and controlling their flow. Obviously complex machines and engines can be produced by the proper joining together of actuator and pumping elements.

An application of a microscopic non-wetting droplet for low friction position control is a microtube liquid-bearing as shown in Figures 33~~A~~a and

33~~B~~b. Referring to Figure 33~~A~~a, for example, the bearing assembly is a microtube with one or more circular channels on its circumference which actually join the microtubes interior void space in a narrow ring-shaped opening. A center rod only slightly smaller in diameter than the bearing assembly is supported by non-wetting fluid filling the circular channels. This fluid cannot leak out around the center rod because too much pressure is required to form the smaller-radius droplet that would be able to leak. The center rod is therefore free to either rotate or translate axially within the bearing assembly. It is referred to as an external bearing because of this outside configuration. The only restraining forces involved are frictional ones between center rod and non-wetting fluid.

Figure 33B illustrates a reciprocal situation, and is referred to as a microtube internal bearing. A straight walled microtube is used. A central rod has at least one groove about the circumference and the non-wetting fluid fills, this groove which allows both rotational and translational motion. Figure 33~~C~~c is a mixed combination of internal and external microtube liquid-bearing locations. In this configuration, however, only rotational motion is easily achieved. For translation to occur, shearing of wetting droplet must take place. While this is not as difficult as forming a small-radius annular droplet, ~~I~~it still involves generation of new droplet-surface area, and therefore requires more force to produce translation than for either the purely internal or purely external bearings.

Figure 34 illustrates a microtube liquid-bearing that will not allow significant translational motion. It is a thrust bearing utilizing four separate microtube liquid-bearings in an external configuration. As before, an internal or mixed configuration is also possible, and additional microtube liquid bearings utilizing surface-tension/wettability effects can be employed.

Figure 35 illustrates how the non-wetting droplet can be employed as an actuator, its motion down a microchannel or microtube being used to move a loosely-fitting piston. It is important to note that as long as the piston and walls are non-wetting to the droplet, none of the droplet will squeeze by the piston if the clearance is less than the non-wetting droplet radius. The non-wetting droplet is shown only in part in Figure 35. That is done deliberately to demonstrate that the actual mechanism, i.e. external stimuli, internal stimuli, wetting fluid, etc, causing it to push on the piston is unimportant. Its ability to function as a mechanical means of transmitting force and thereby performing work is all that matters.

CONCLUSIONS

Microtubes appear to have almost universal application in areas as diverse as optics, electronics, medical technology, and micro-electromechanical devices. Specific applications for microtubes are as diverse as chromatography, encapsulation, cross- and counter-flow heat exchange, injectors, micro-pipettes, dies, composite reinforcement, detectors, micropore filters, hollow insulation, displays, sensors, optical wave guides, flow control, pinpoint lubrication, micro-sponges, heat pipes, microprobes, plumbing for micromotors and refrigerators, etc. The technology works equally well for high and low temperature materials and appears feasible for all applications that have been conceived to date.

The advantage of microtube technology is that tubes can be fabricated inexpensively out of practically any material in a variety of cross-sectional and axial shapes in very precise diameters, compositions, and wall thicknesses orders of magnitude smaller than is now possible. In contrast to the other micro- and nano-tube technologies currently being developed, microtubes can be made out of a greater range of materials with a greater range of lengths and diameters, and with far greater control over the cross-sectional shape. These tubes will provide the opportunity to miniaturize (even to nanoscale dimensions) numerous products and devices that are currently in existence as well as allowing the fabrication of innovative new products that have to date been impossible to produce.

Space only allowed the presentation of one application of microtube technology to new innovative products in greater detail. This one application comprised those devices that are based on surface tension and wettability. The few devices that were shown as examples demonstrated the breath of this technology in only one field. The application of microtube technology to other fields is considered to be equally rich and limited only by a designer's imagination.

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FIGURE CAPTIONS

Figure 1. Examples of microtubes. (a) 10 micron silicon carbide tubes. (b) 410 micron nickel tubes. (c) 26 micron silicon nitride tube. (d) 0.6 micron quartz tube.

Figure 2. Above 1 micron inside diameter tubes can be made in any cross-sectional shape such as (a) 17 micron star, (b) 9 X 34 micron oval, (c) 59 micron smile, and (d) a 45 micron trilobal shape.

Figure 3. Tubes can be structurally sound with very thin walls (a) or with thick walls (b). etc.

Figure 4. Microtube with porous tube wall.

Figure 5. (a) Sapphire tube with silver liner. (b) Nickel tube with a silver liner.

Figure 6. Solid nickel structure with oriented micro-channels.

Figure 7. Examples of a curved silver tubes. (a) Single tube (b) Multiple tubes.

Figure 8. (a) Section of "large" coiled tube. (b) Open end of coiled tube.

Figure 9. A coiled tube wrapped around a tube or fiber that can be used as a heat exchanger or as a microscopic screw-drive.

Figure 10. (a) A conventional round bellows. (b) A straight bellows with a square cross-section. (c) A square bellows with a twist. (d) A tapered square camera bellows with a sun shade to demonstrate the versatility of the technique. (e) A round bellows with a dove-tail connector.

Figure 11. Microtube bellows finger. a.) unpressurized b.) pressurized

Figure 12. Different ways of transitioning microtubes to the real world. (a) taper (b) telescope (c) bundle (d) manifold.

Figure 13. (a) A thin-walled 5-micron I.D. tube telescoped to a 250-micron O.D. tube. (b) View of the small open end of the telescope.

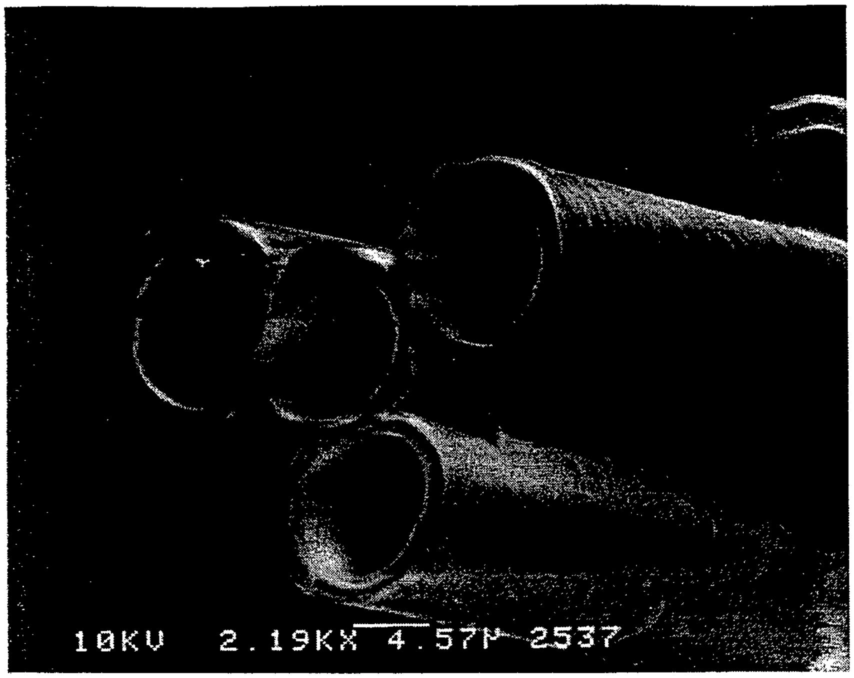


Fig 1a

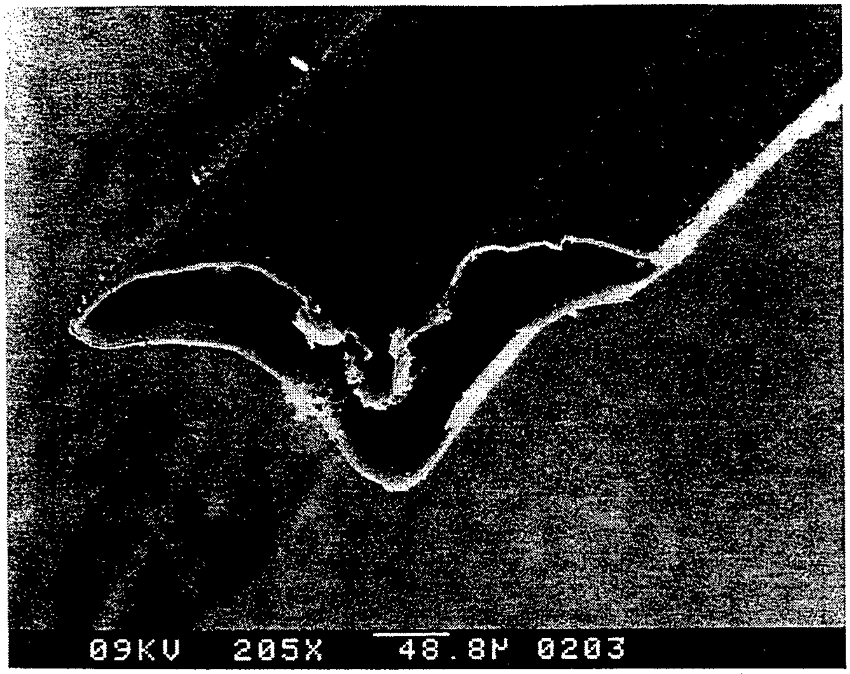


Fig 1b

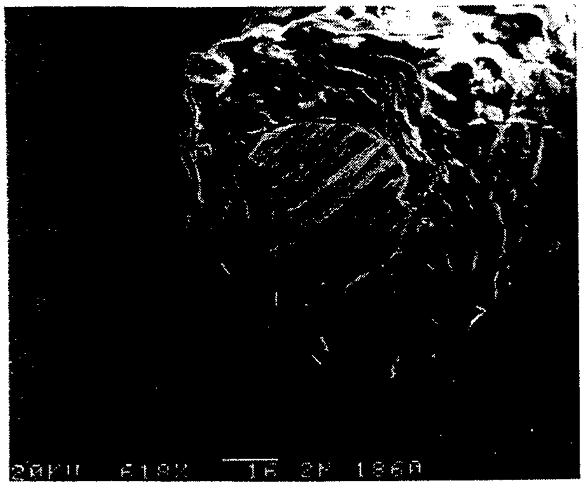


Fig 1c

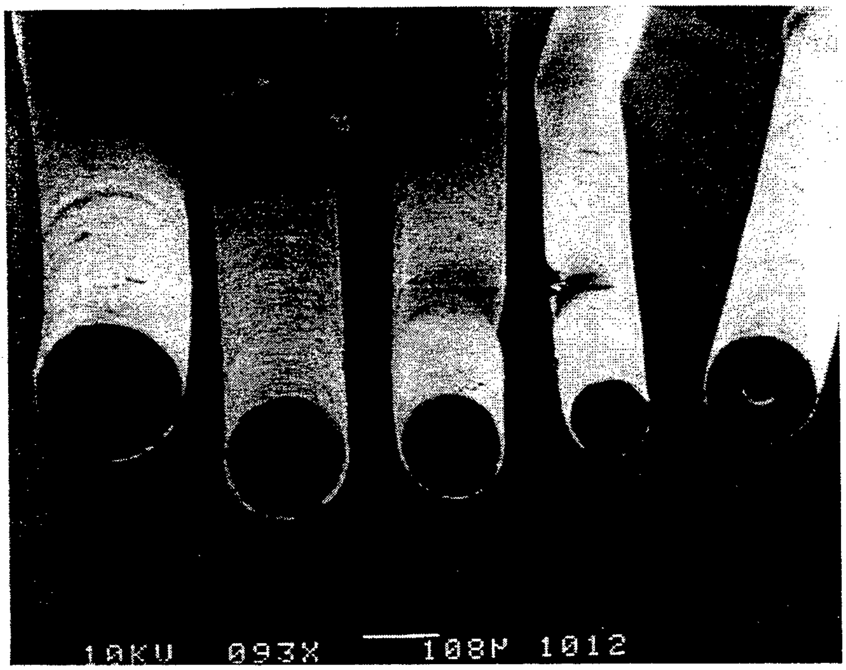


Fig 1 d

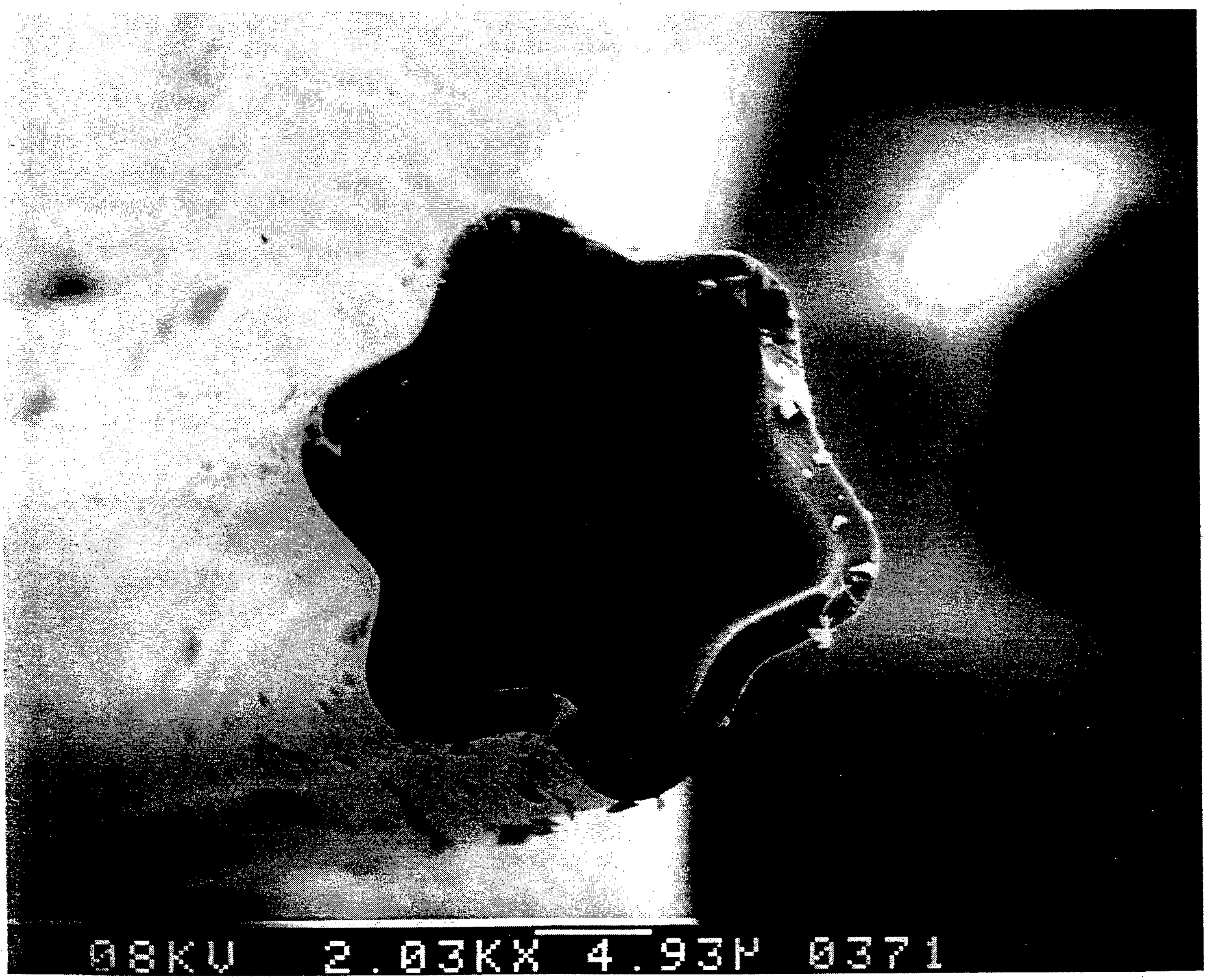


Fig 2a

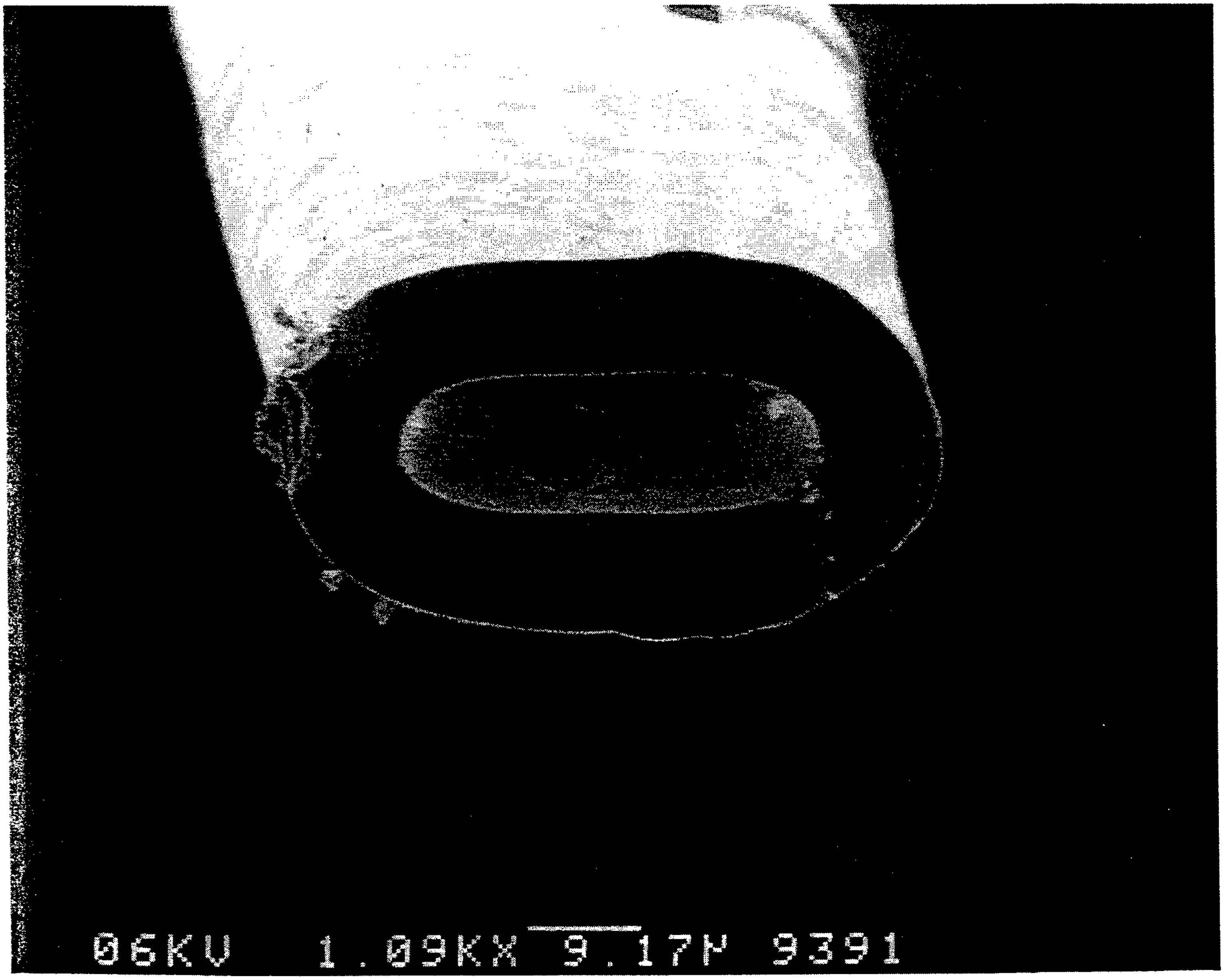


Fig 2b

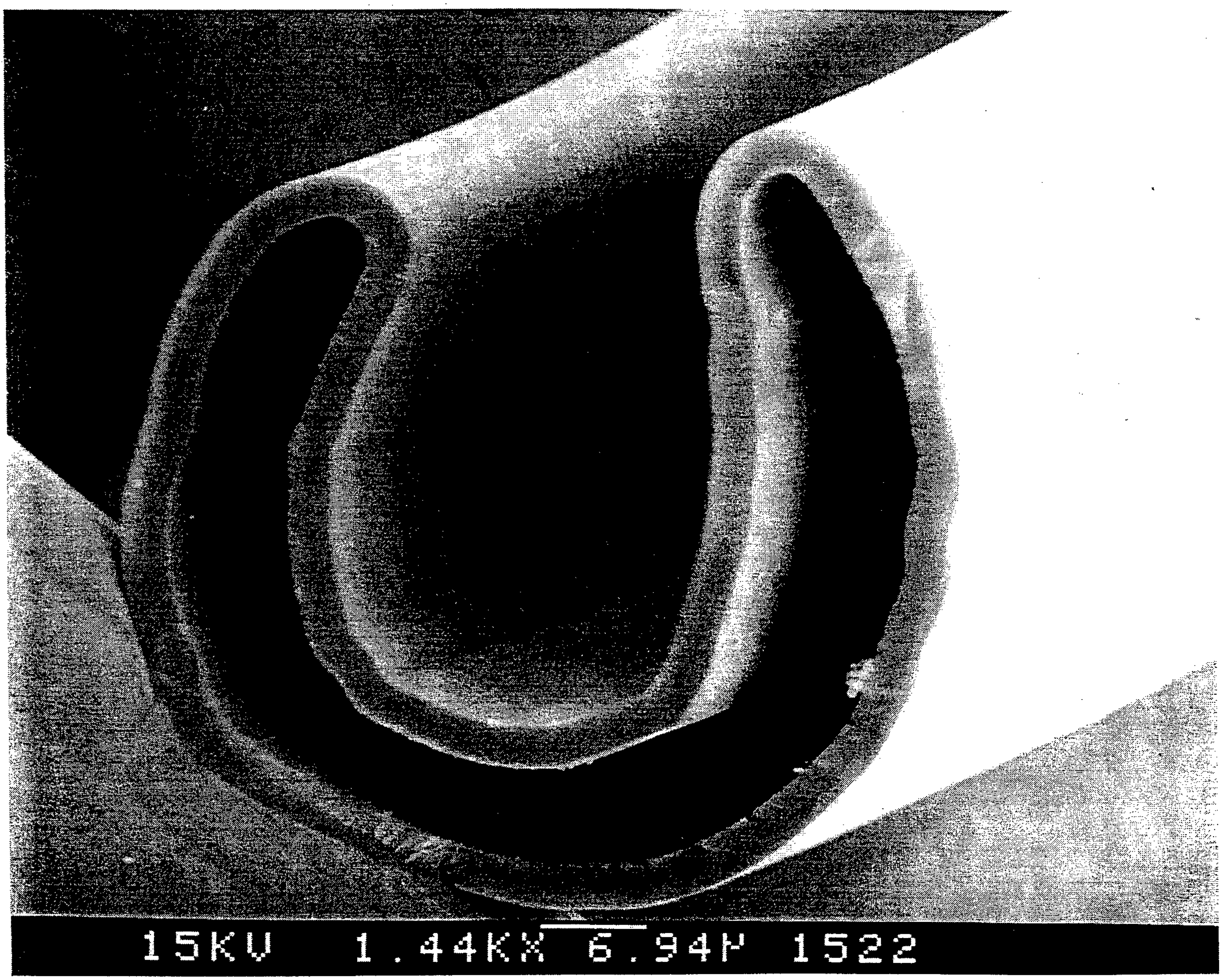


Fig 2c

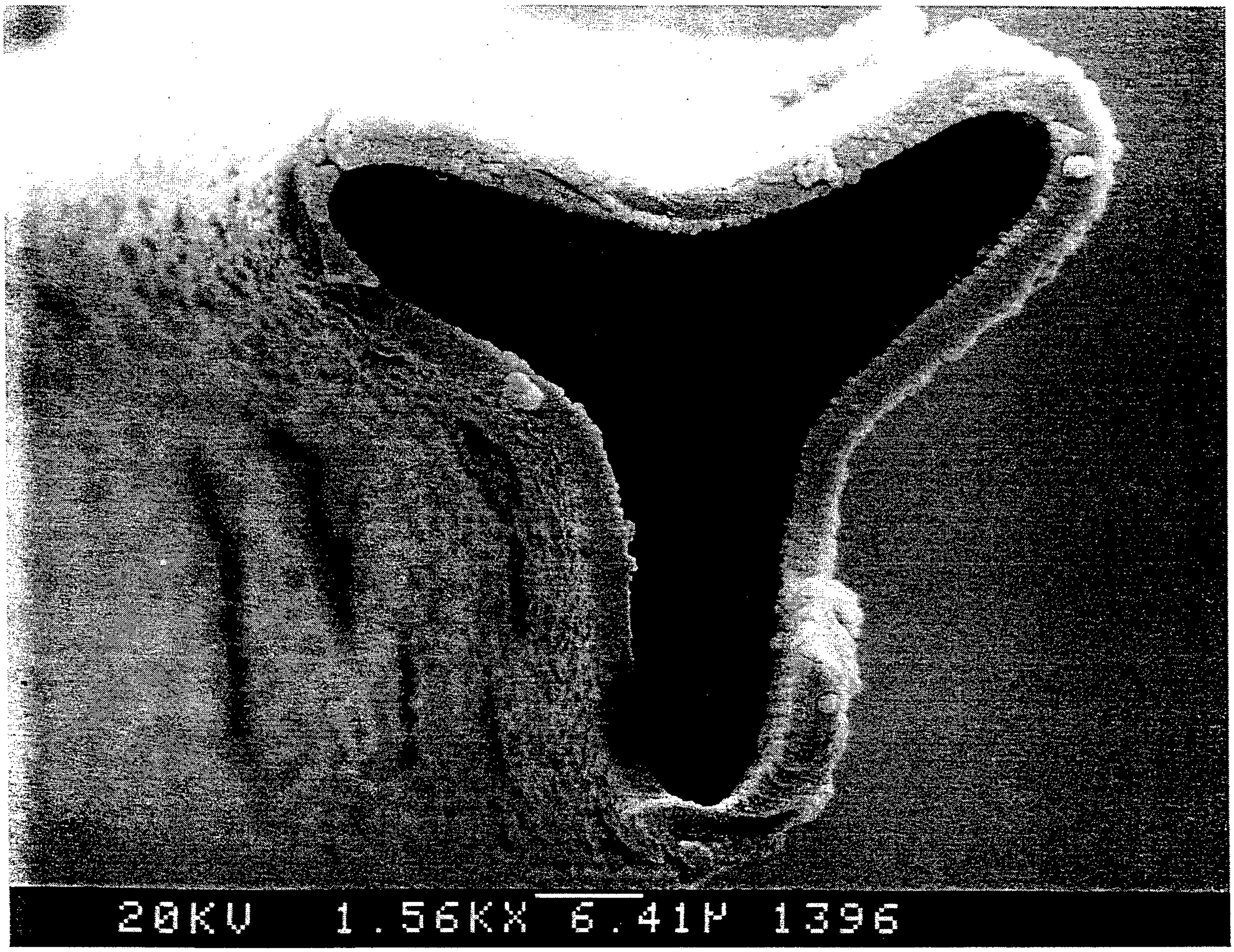


Fig 2d

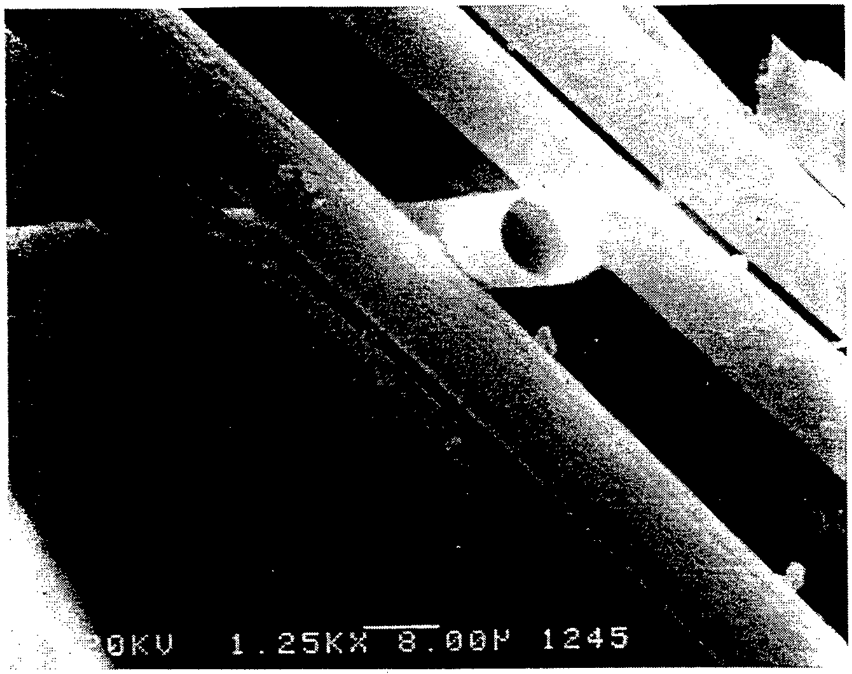


Figure 3a

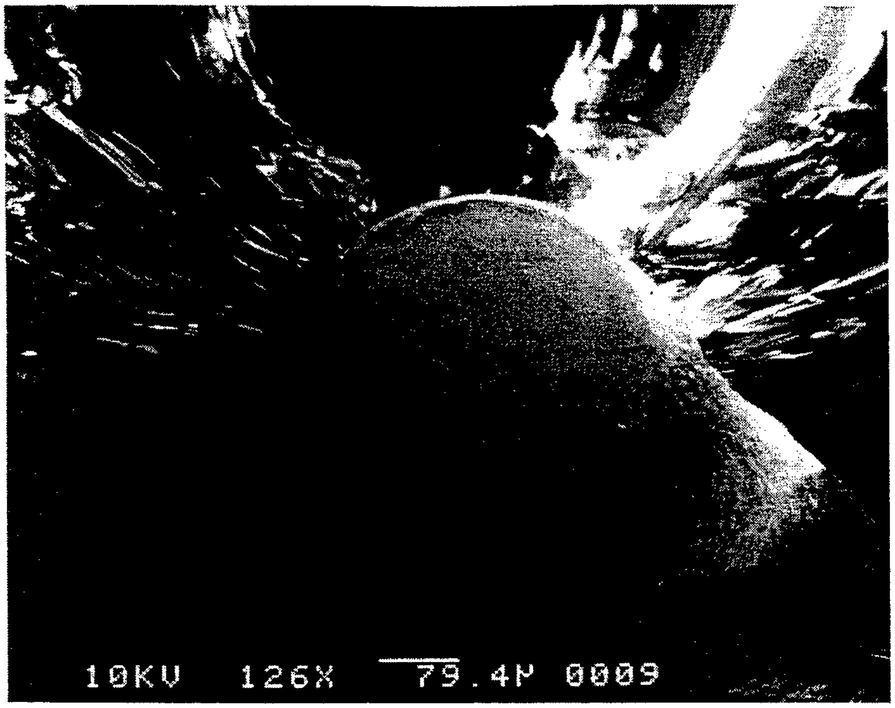


Figure 3B

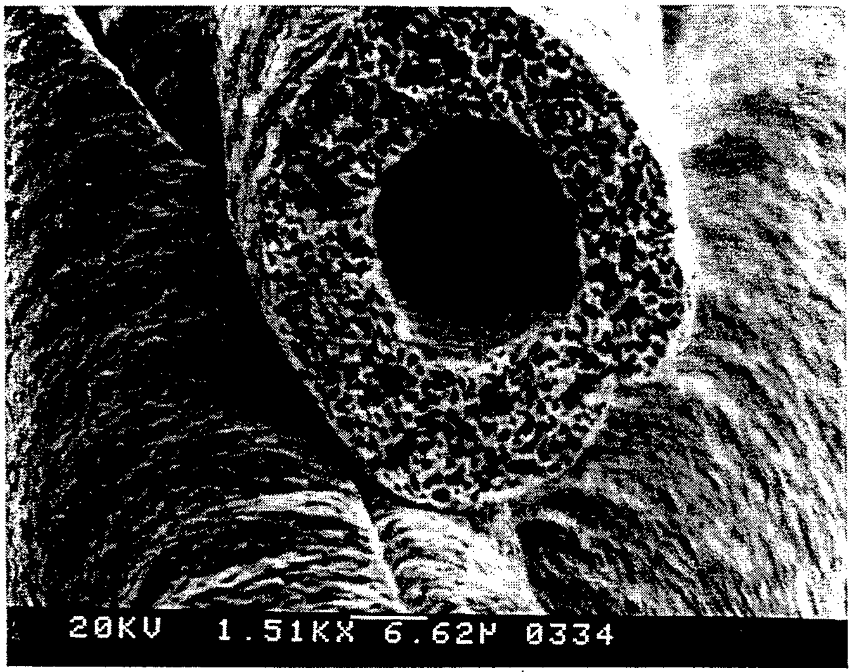


Figure 4

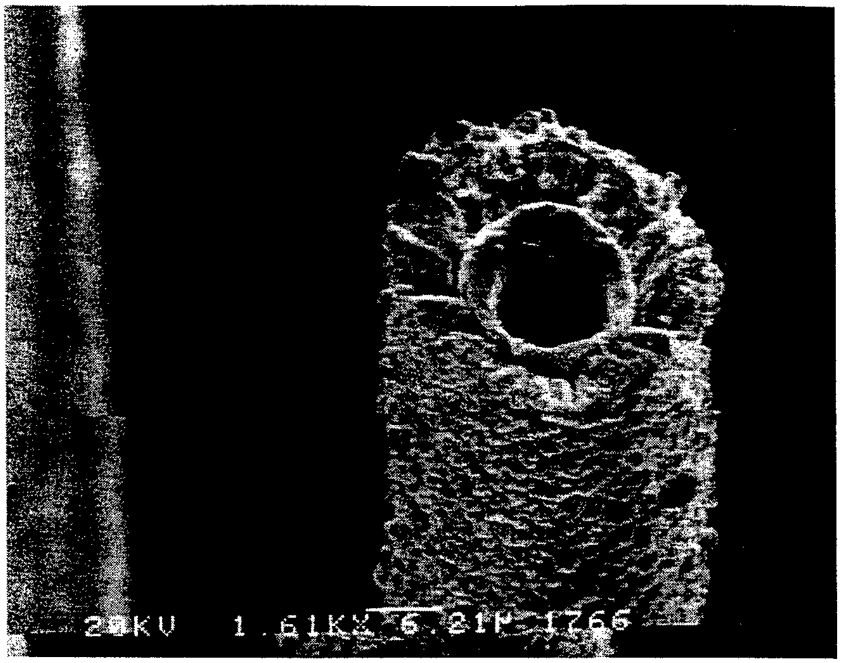


Fig 5a

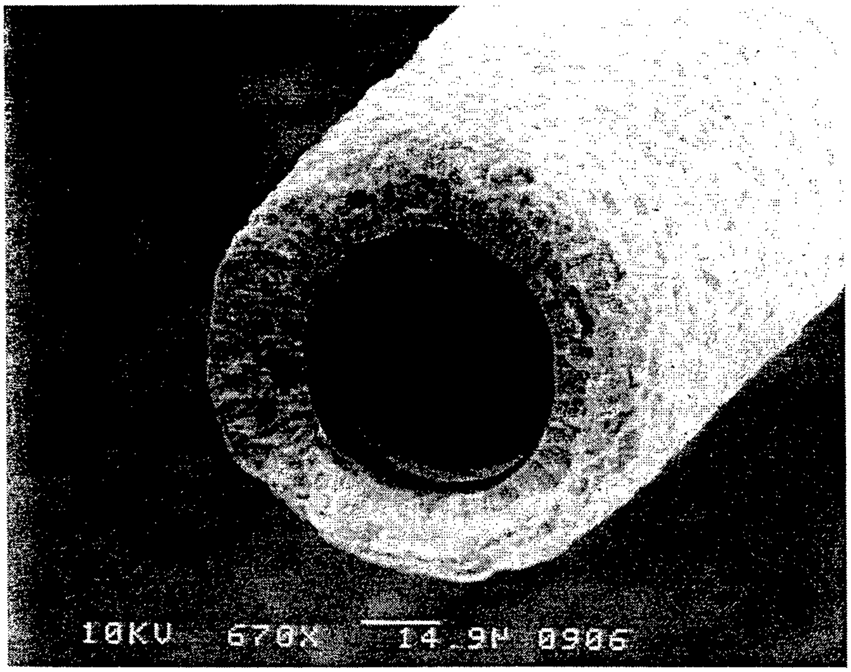


Fig 5b

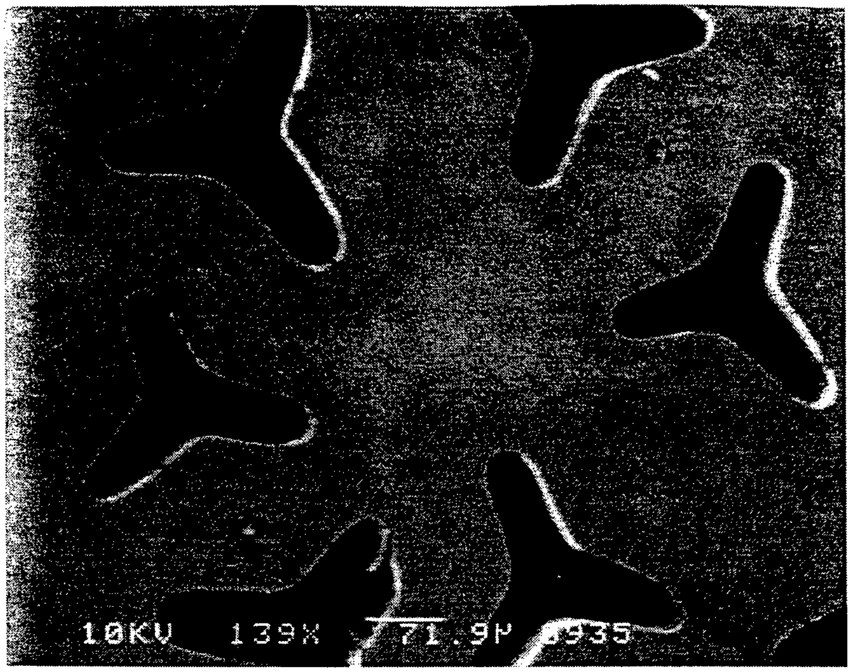


Fig 6

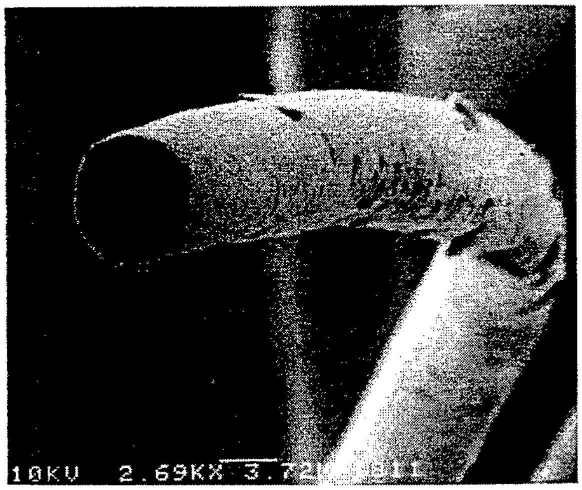


Figure 7a

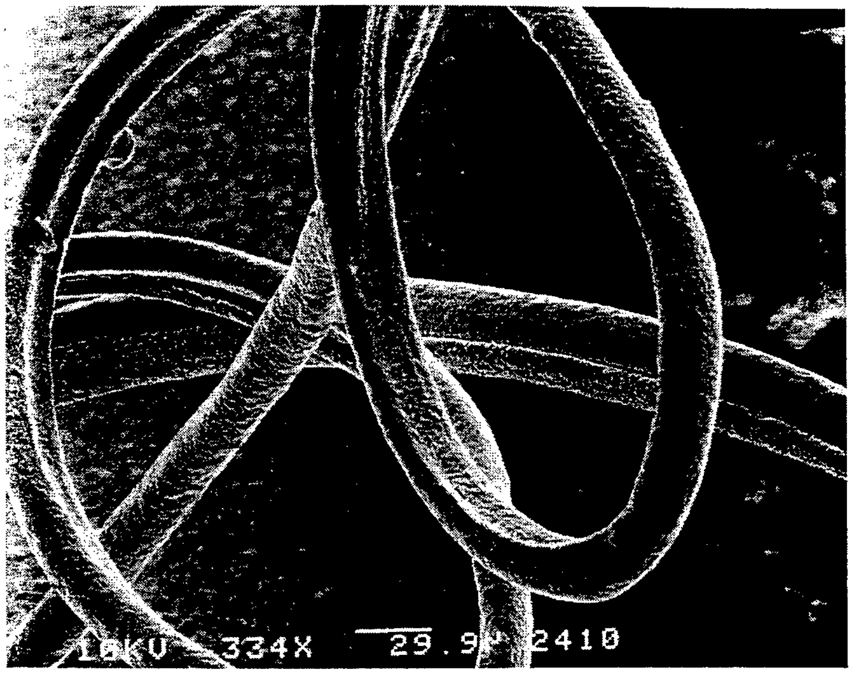


Fig 7D

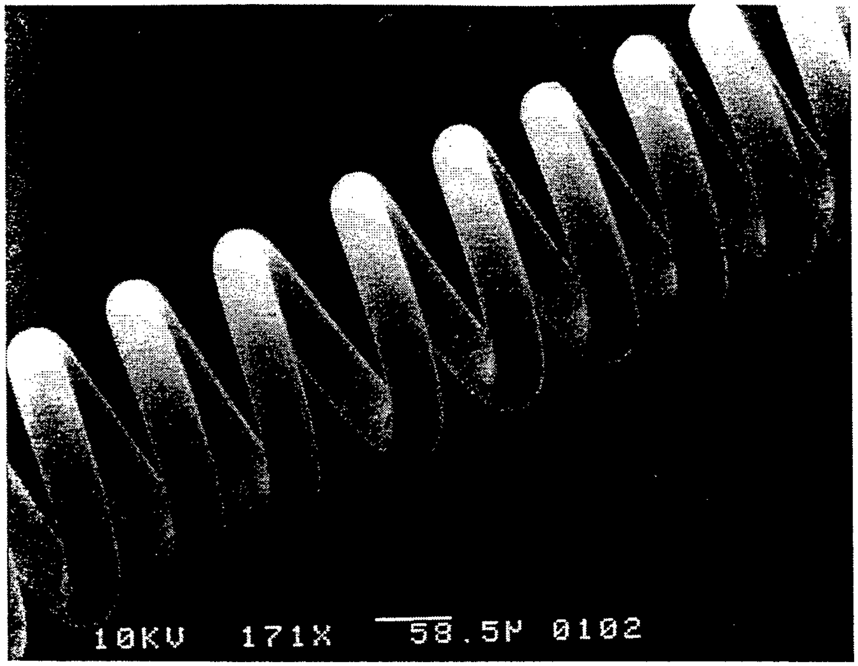


Fig 8a

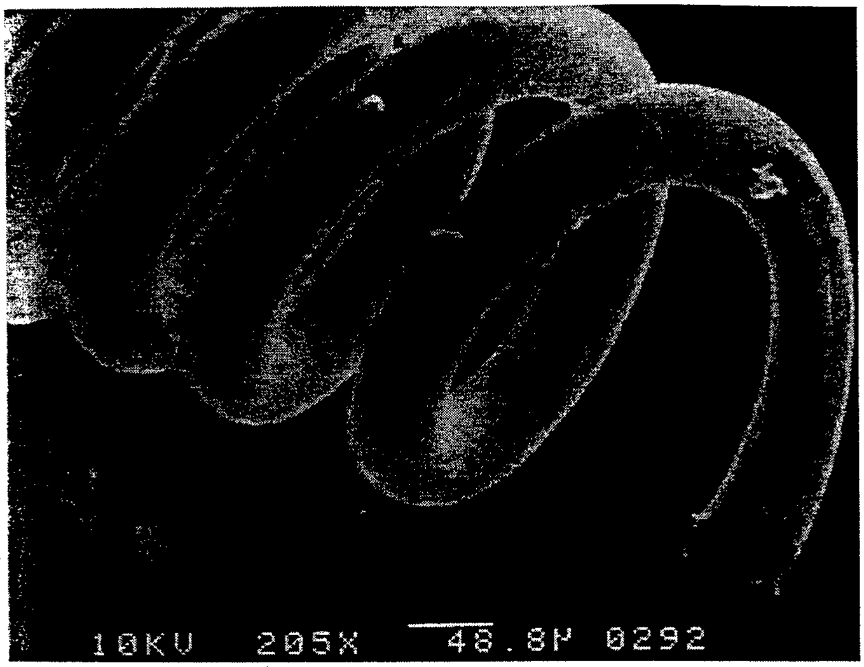


Fig 8b

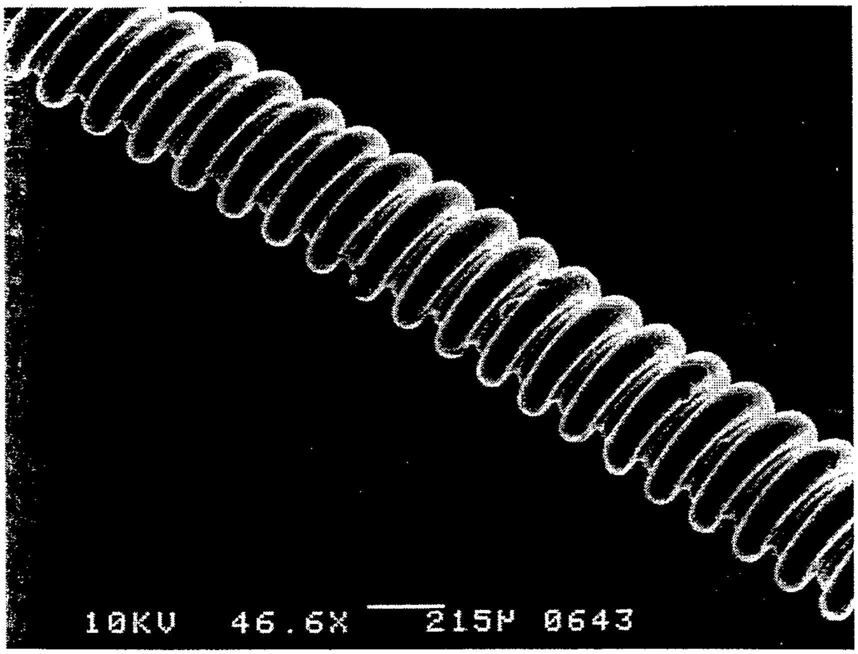


Fig 9

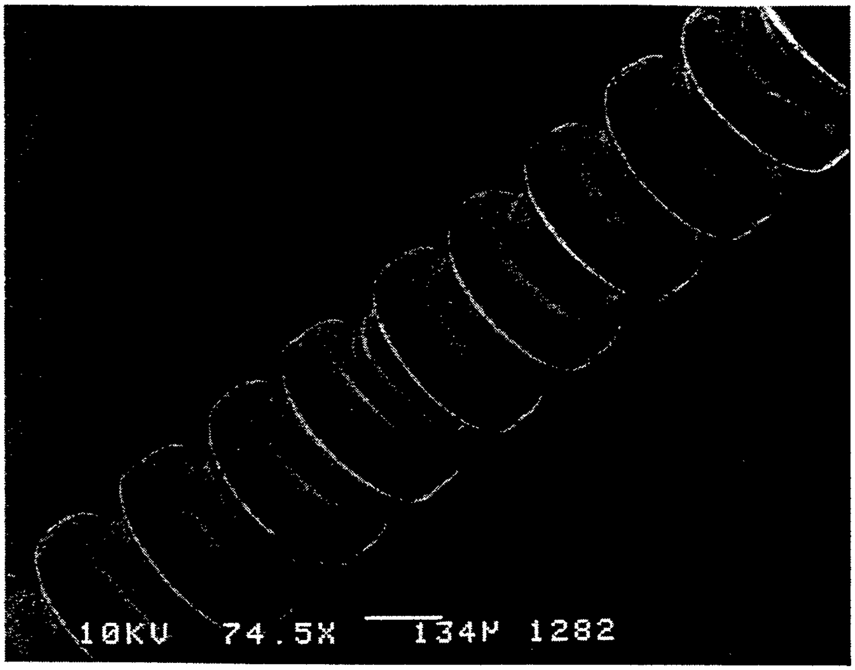


Fig 10a

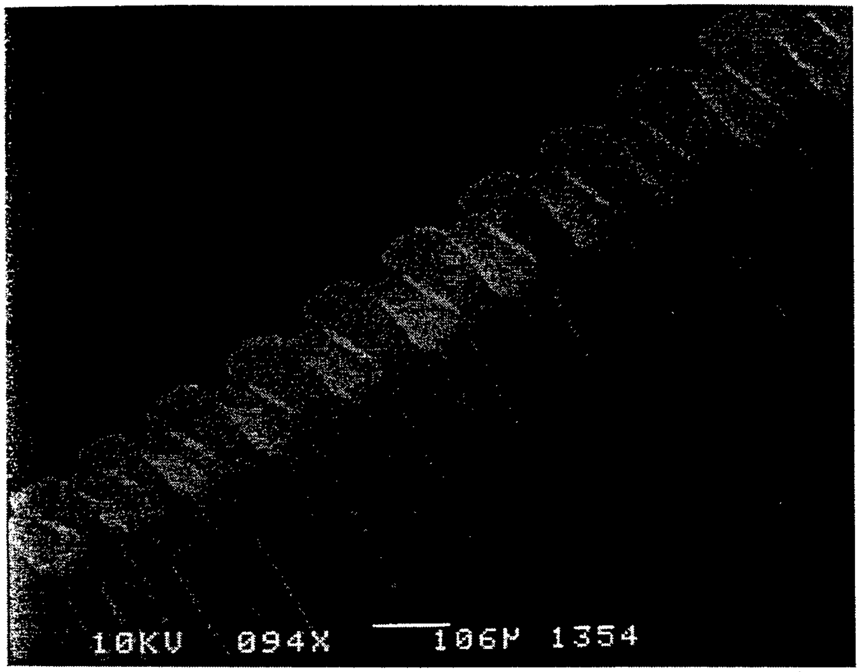


Fig 10b

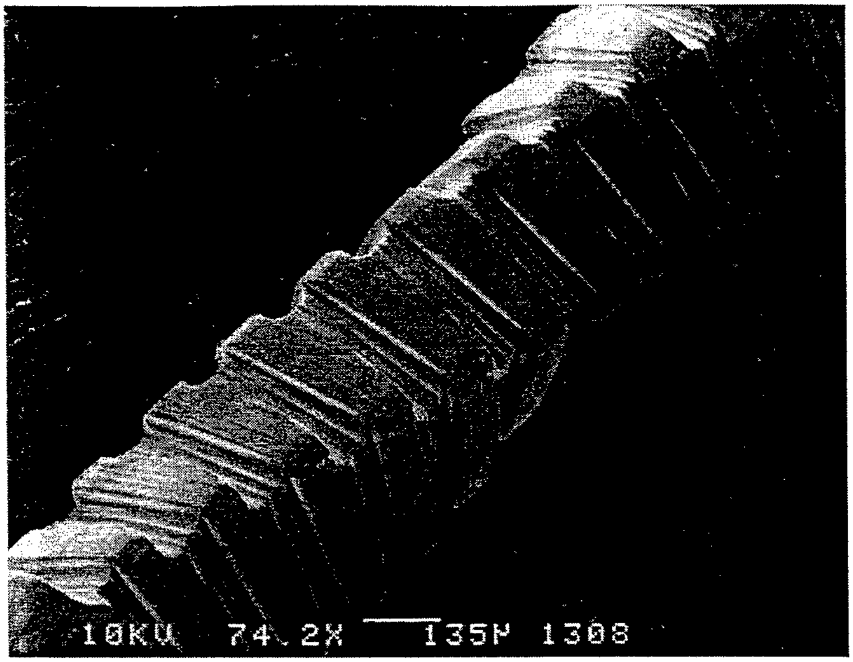


Fig 10C

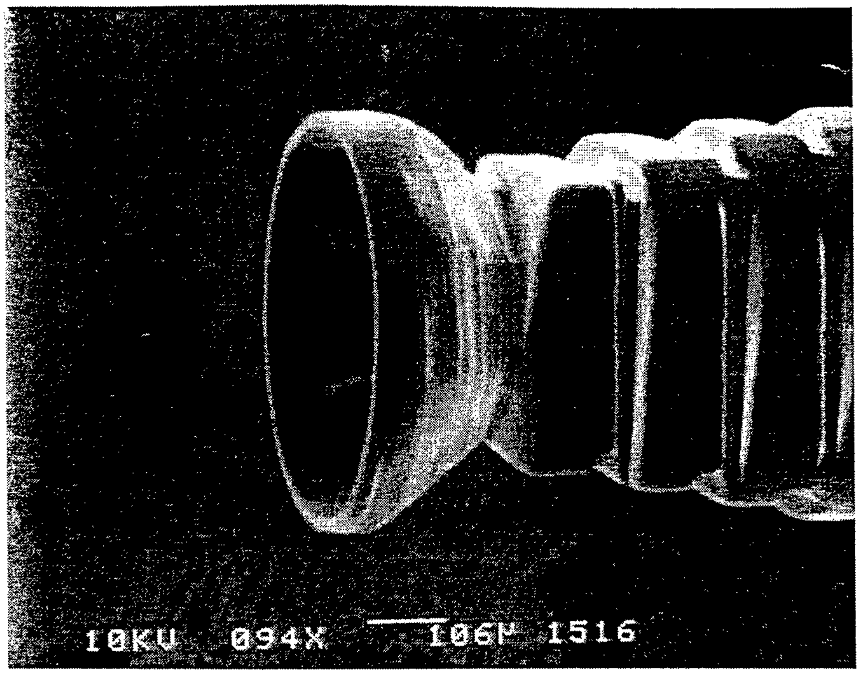


Fig 10d

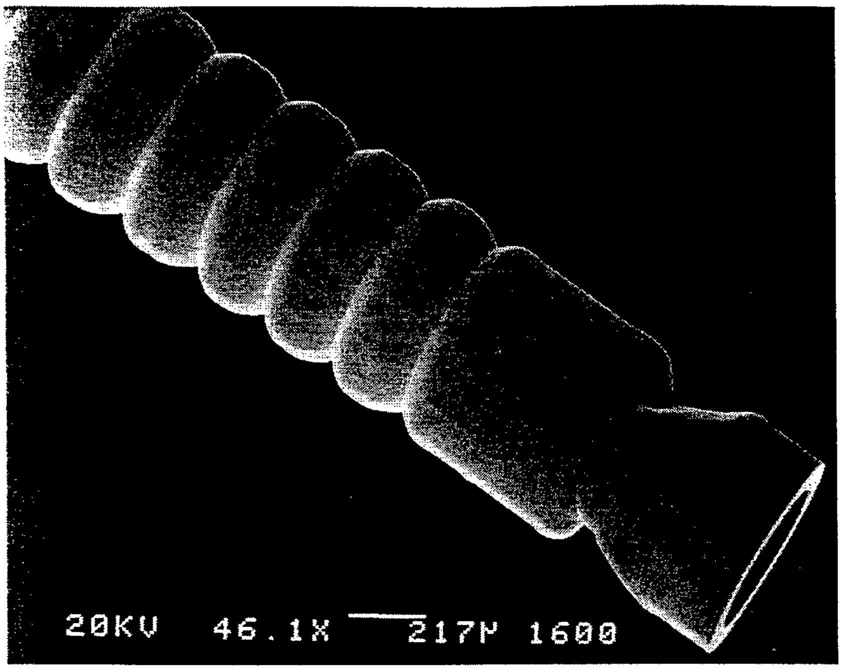


Fig 10e

FIG. 11A

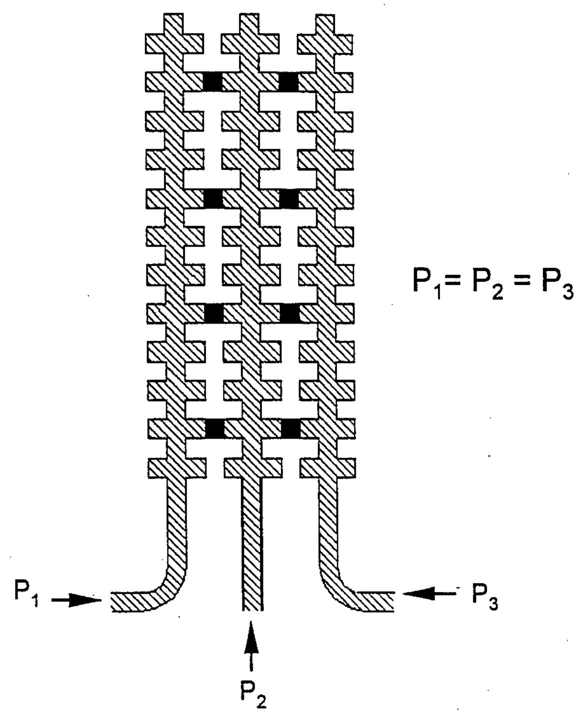
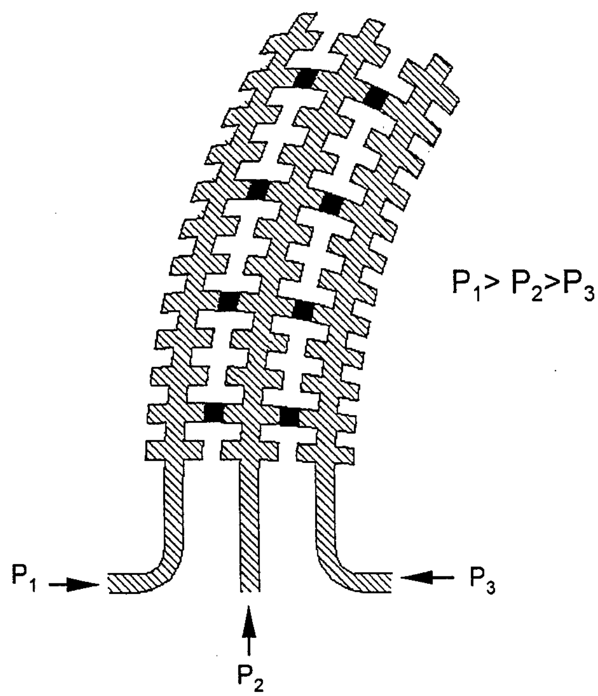


FIG. 11B



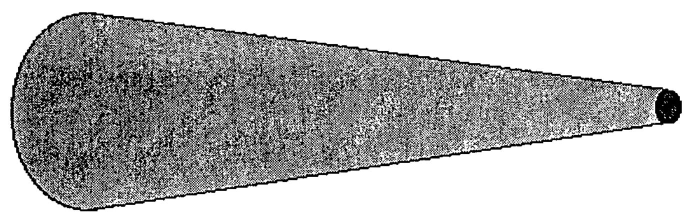


Fig. 12 a

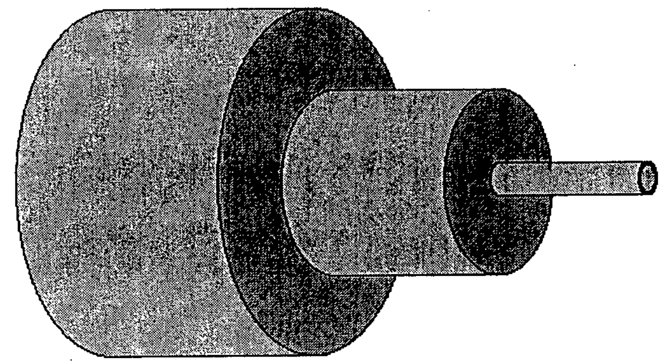


Fig 12 b

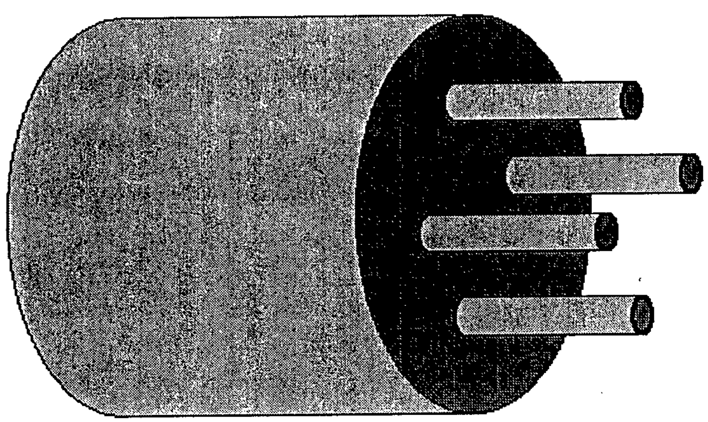


Fig 12 c

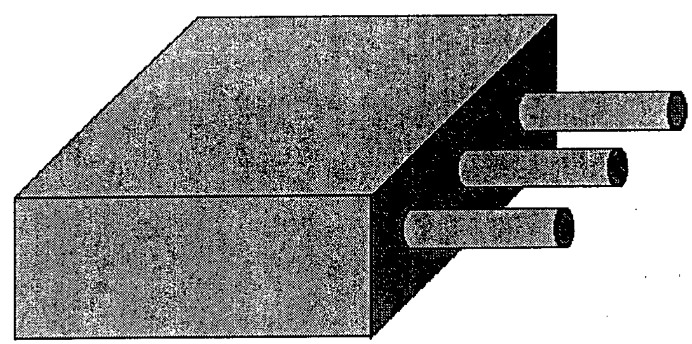


Fig 12 d

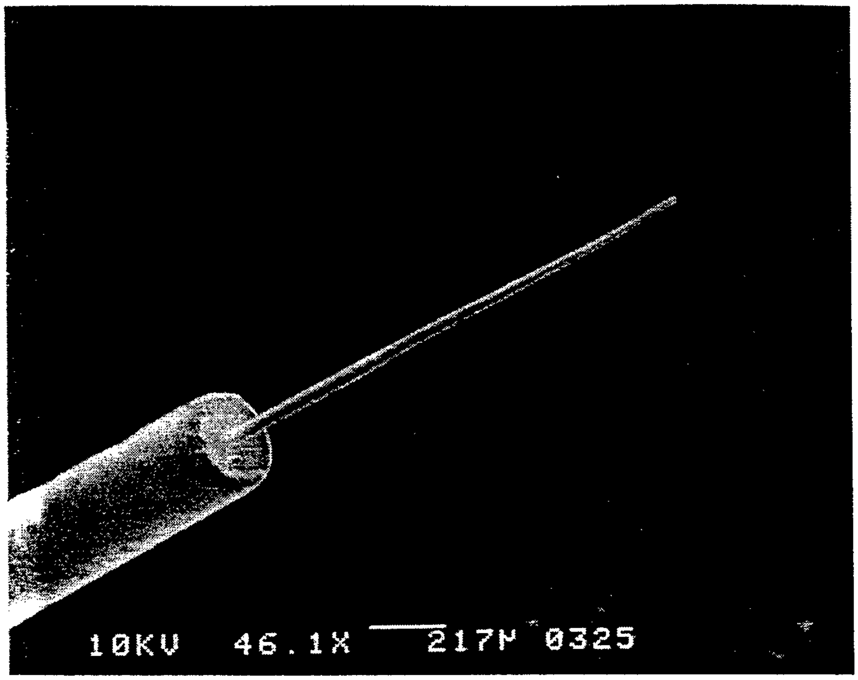


Figure B4

13B

Figure 14

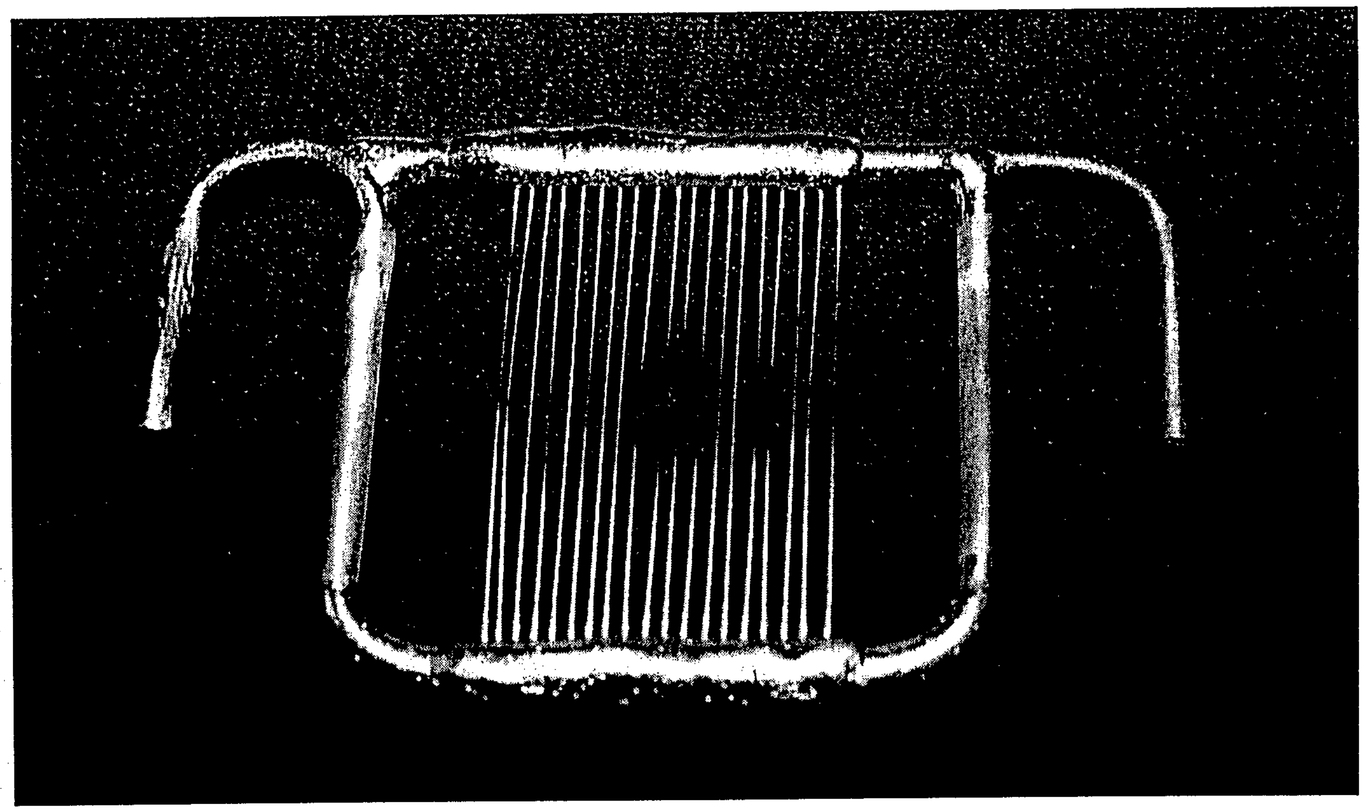


FIG. 15a

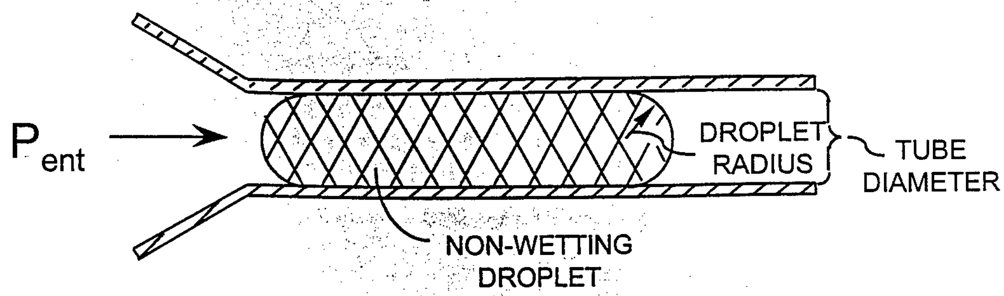


FIG. 15b

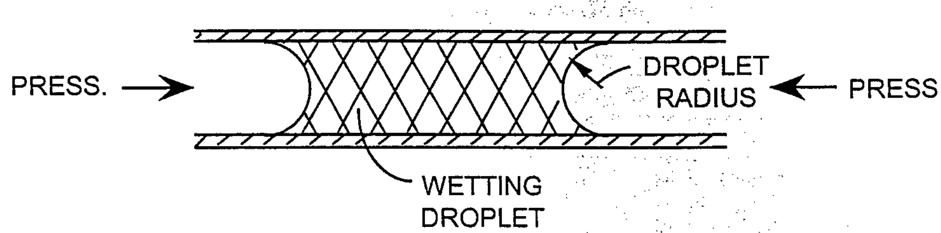


FIG. 16A

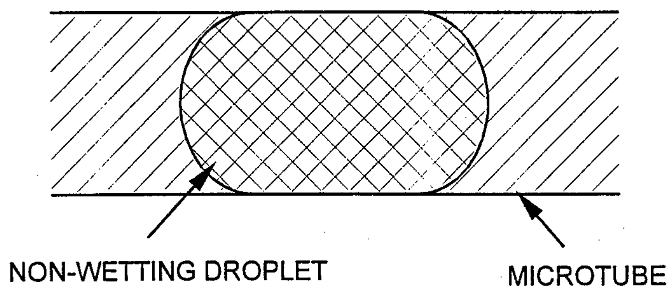


FIG. 16B

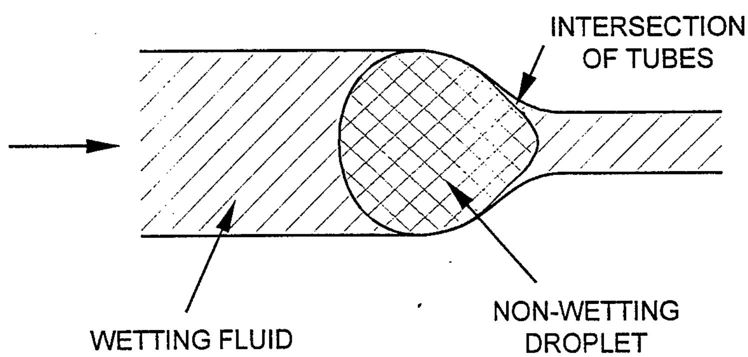


FIG. 17A

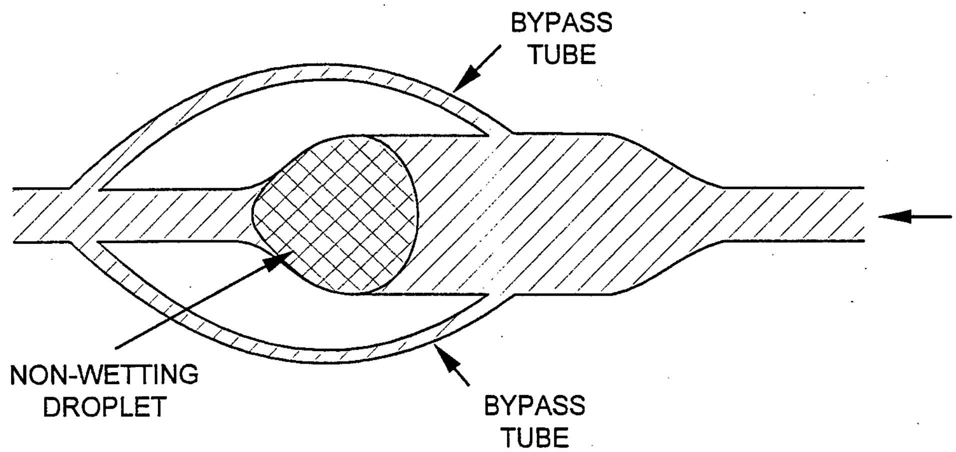


FIG. 17B

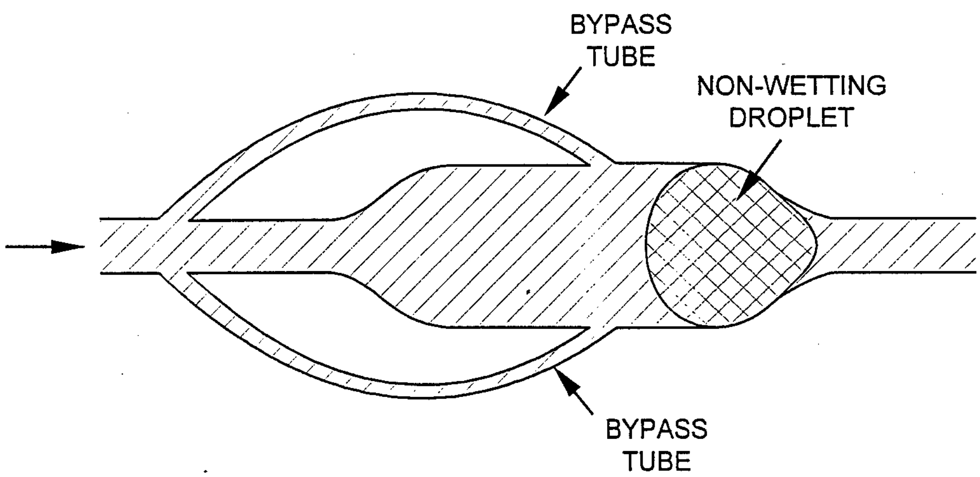


FIG. 18

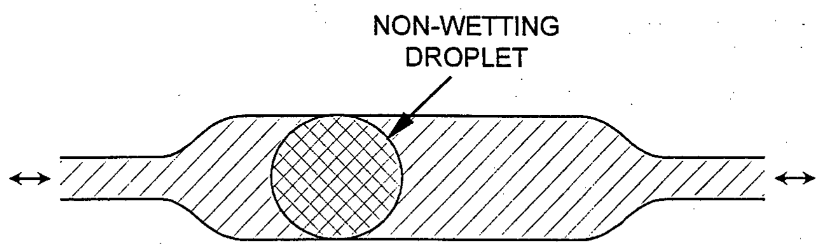


FIG. 19

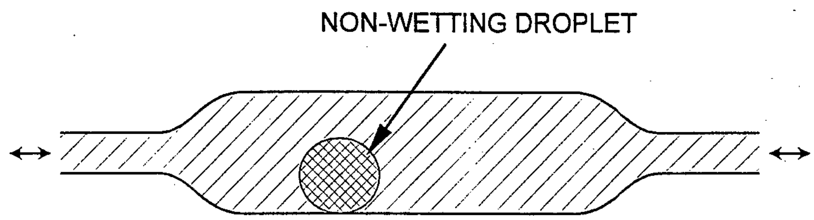


FIG. 20

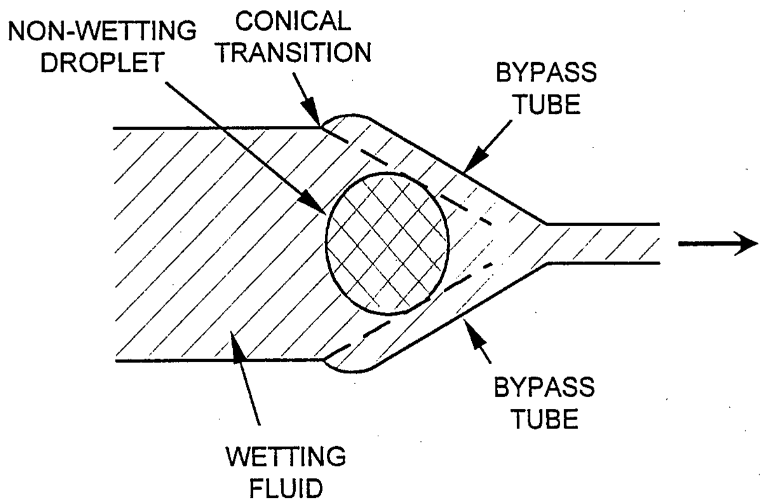

NON-WETTING DROPLET
CONICAL TRANSITION
BYPASS TUBE
BYPASS TUBE
WETTING FLUID

FIG. 21A

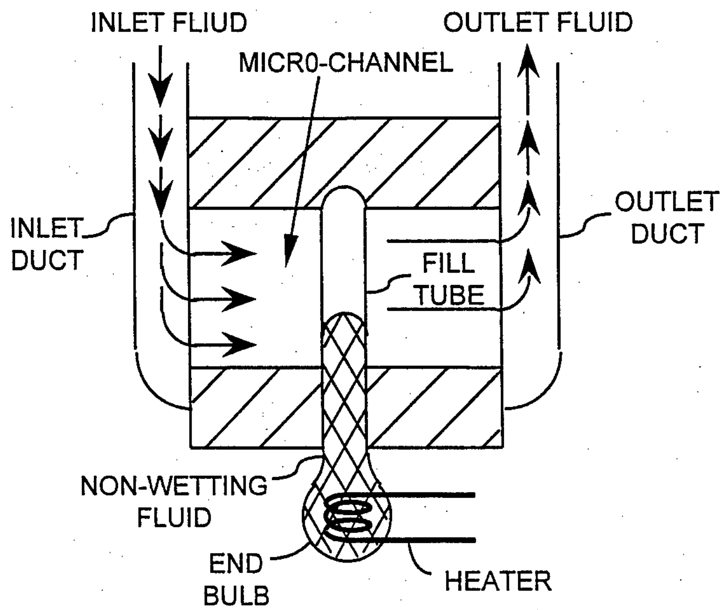


FIG. 21B

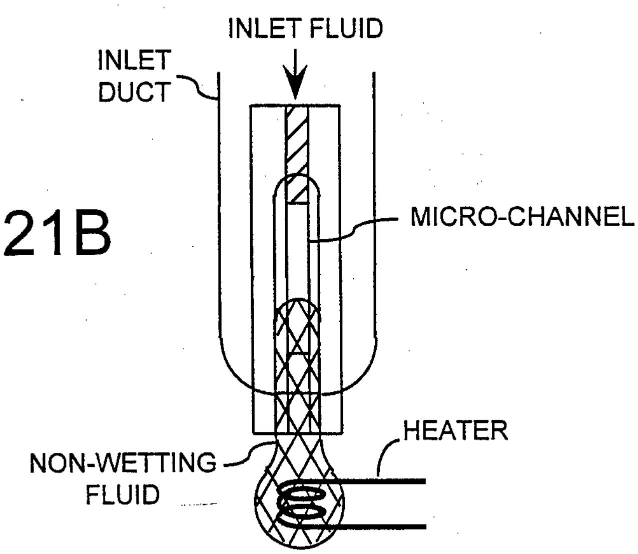
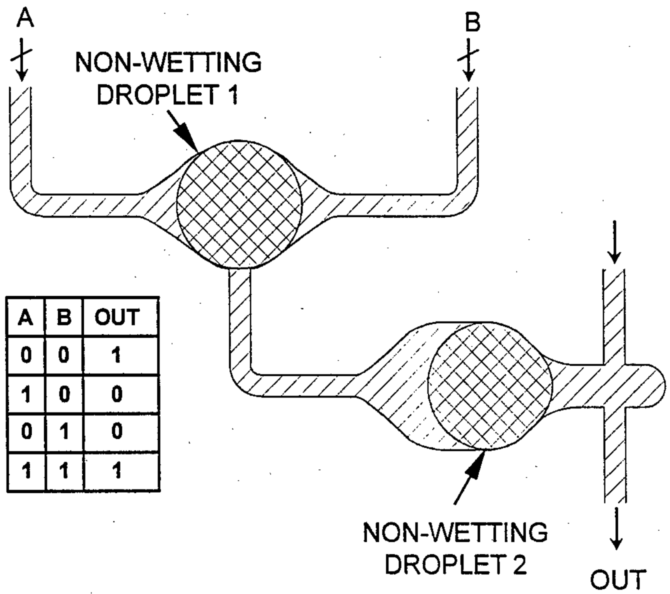


FIG. 22A



A	B	OUT
0	0	1
1	0	0
0	1	0
1	1	1

FIG. 22B

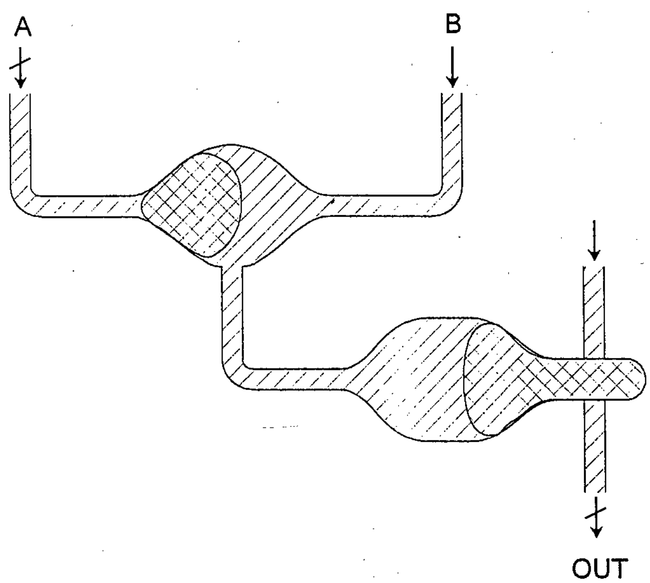
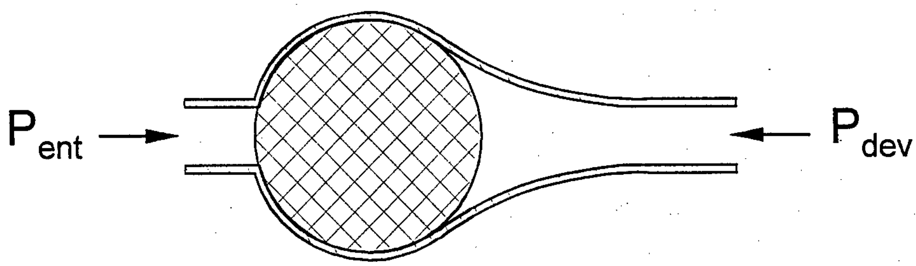
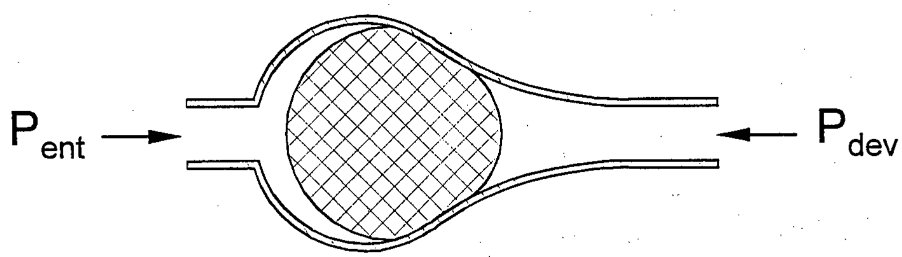


FIG. 23A



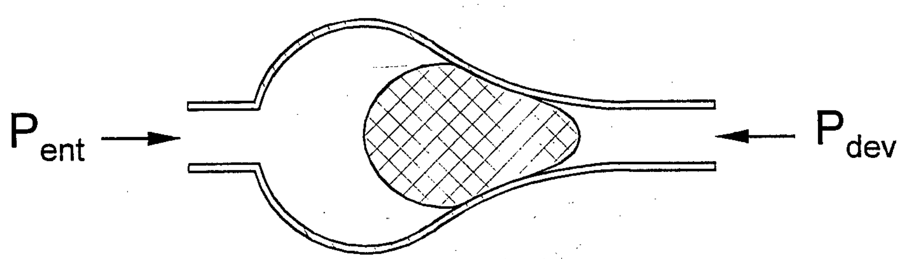
$P_{ent} = P_{dev}$

FIG. 23B



$P_{ent} > P_{dev}$

FIG. 23C



$P_{ent} >> P_{dev}$

FIG. 24

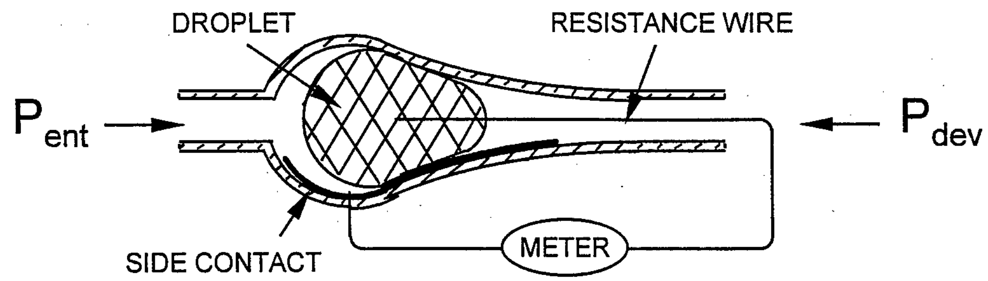


FIG. 25A

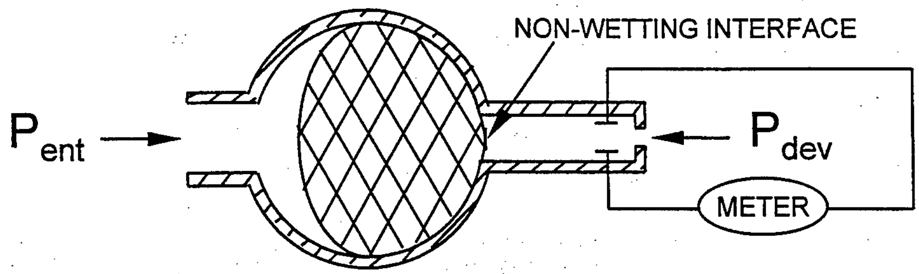


FIG. 25B

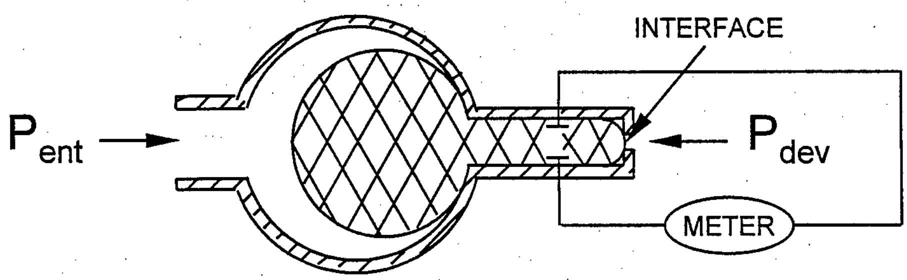


FIG. 26

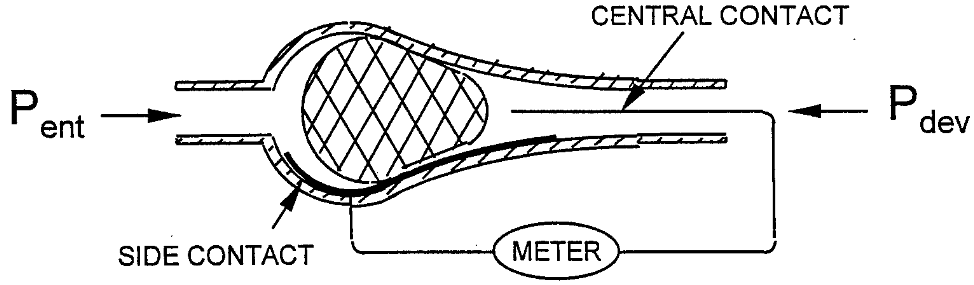
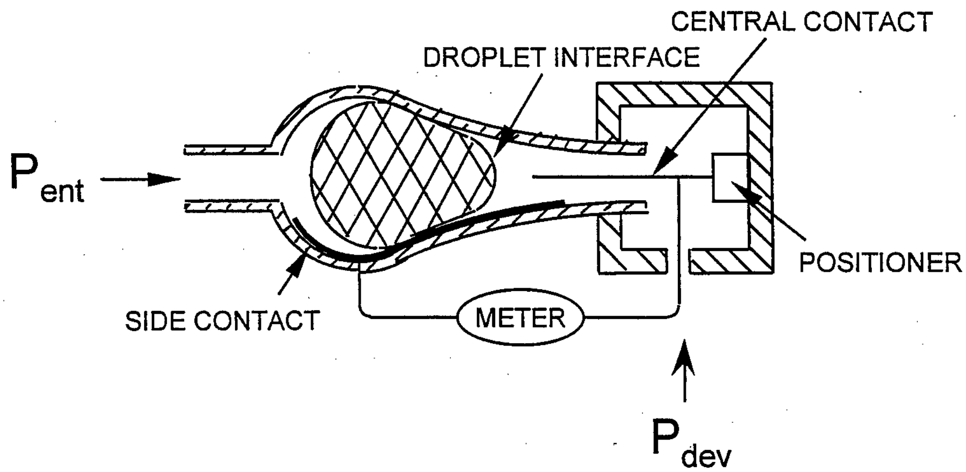


FIG. 27



CENTRAL CONTACT
DROPLET INTERFACE
P_{ent}
POSITIONER
SIDE CONTACT
METER
P_{dev}

FIG. 28

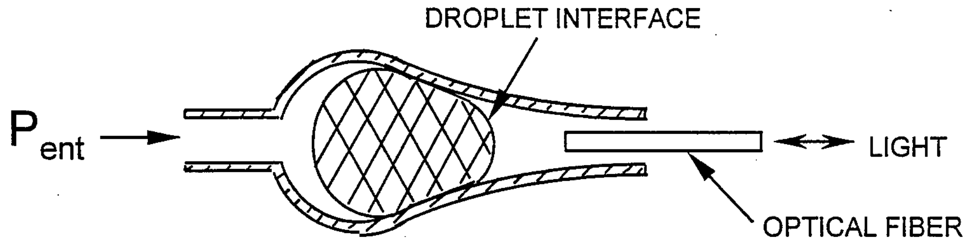


FIG. 29

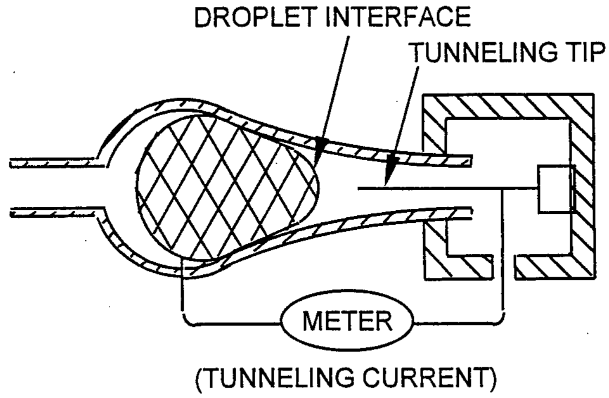


FIG. 30A

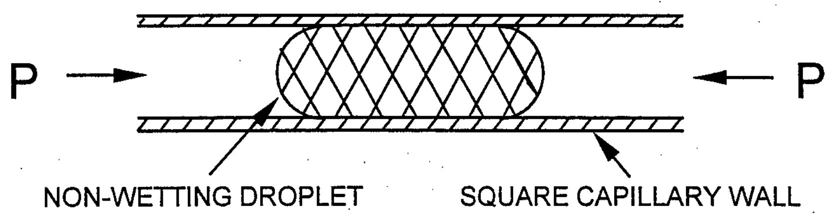


FIG. 30B

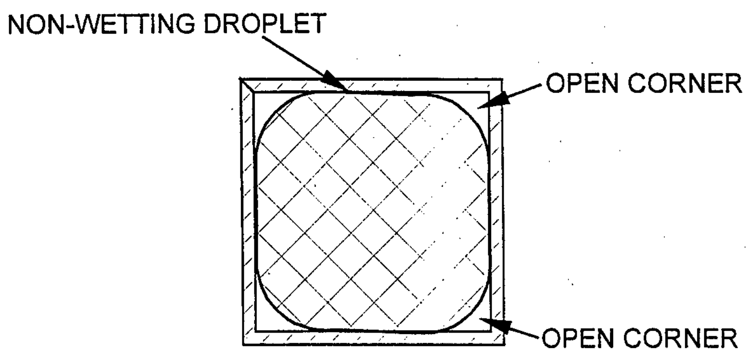


FIG. 31A

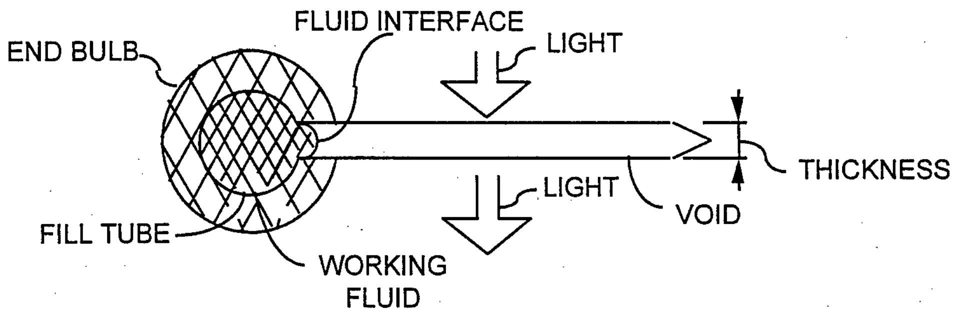


FIG. 31B

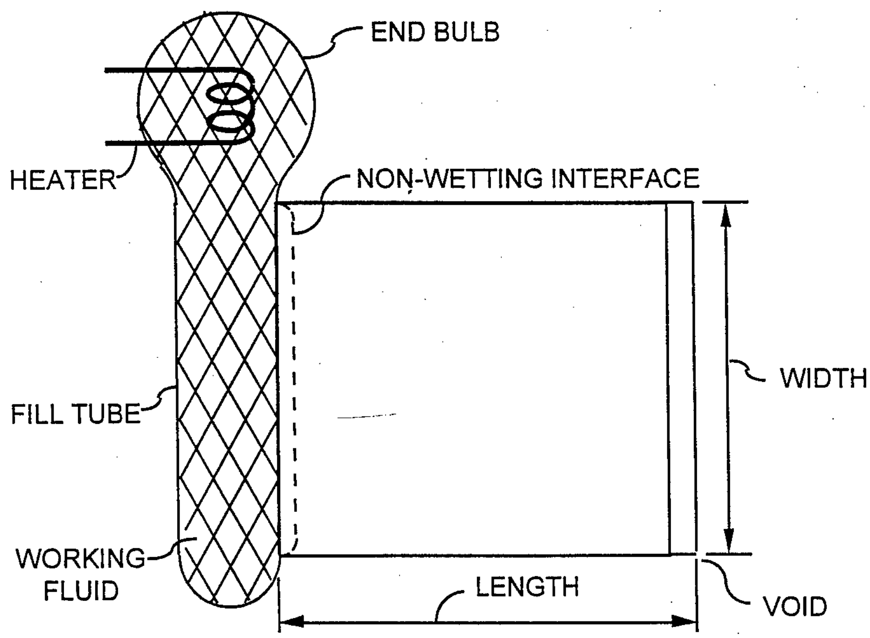


FIG. 31C

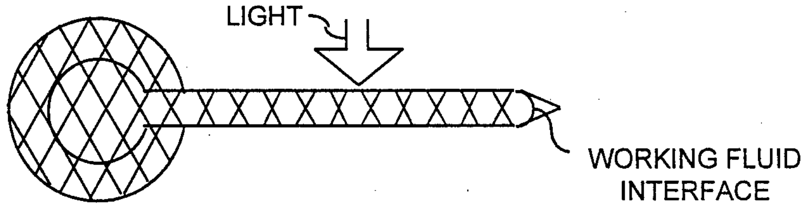


FIG. 31D

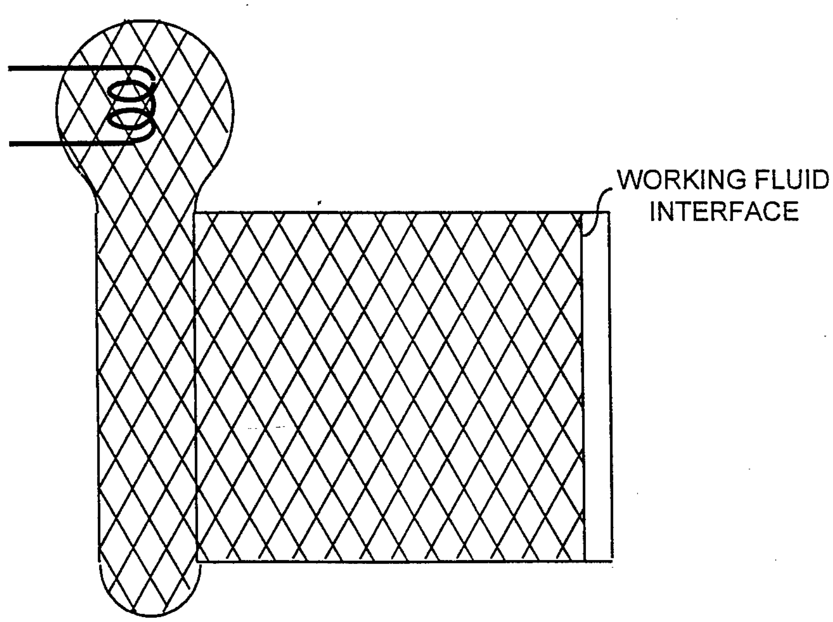


FIG. 32A

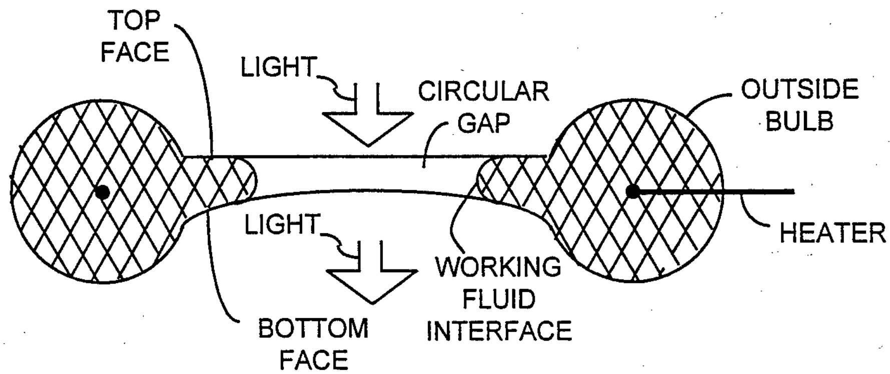


FIG. 32B

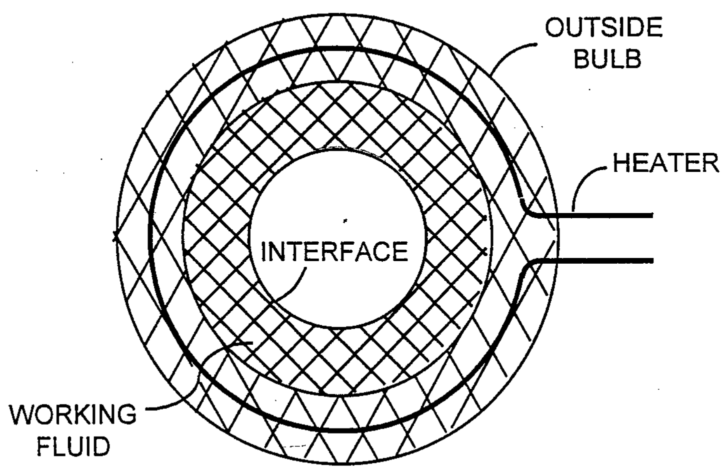


FIG. 33A

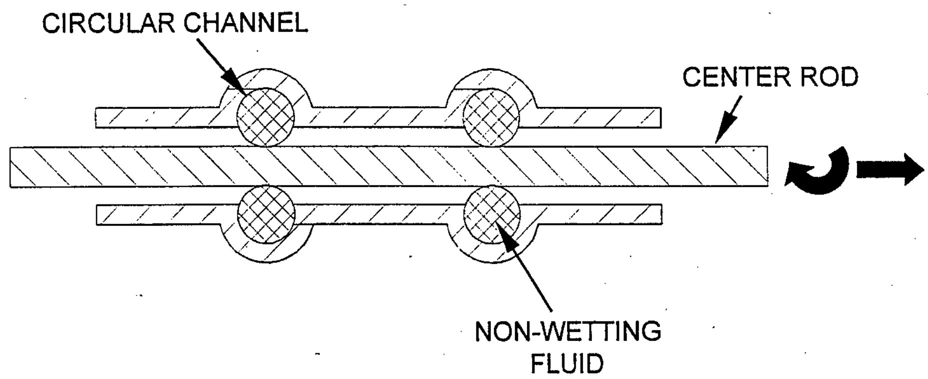


FIG. 33B

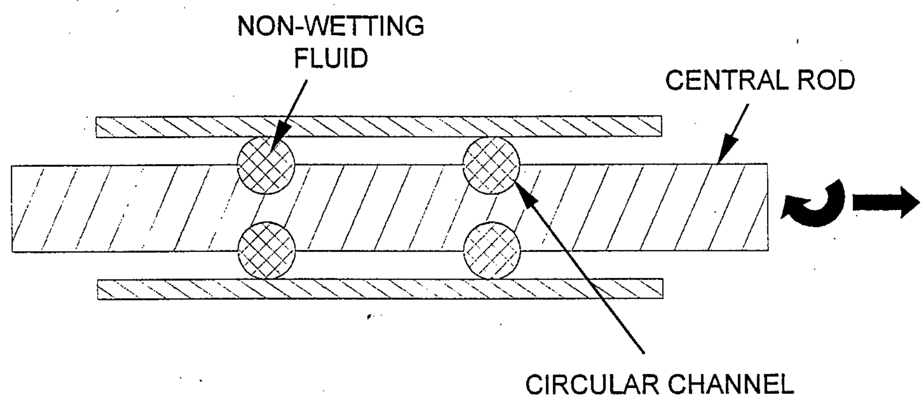


FIG. 33C

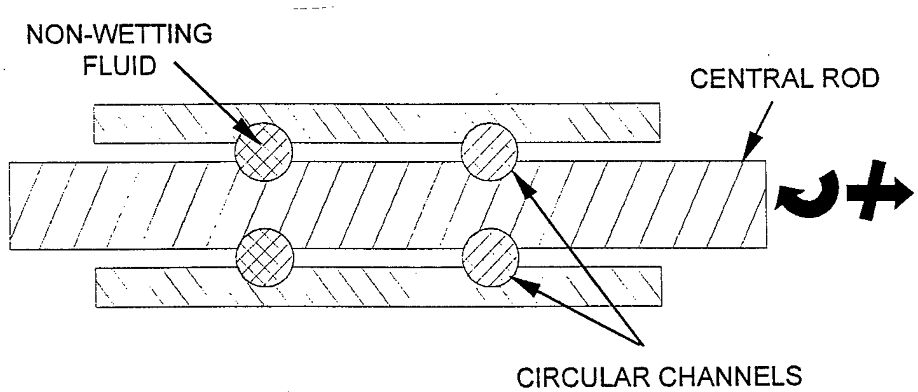


FIG. 34

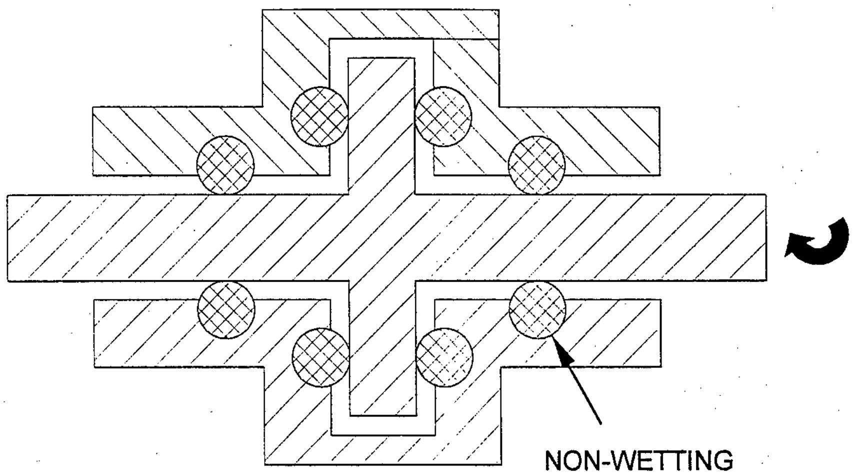


FIG. 35